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IV.—CONCERNING THE PENTAGLUCOSES.

BY W. E. STONE.

The two isomeric sugar-like bodies, arabinose and xylose, with the common formula $C_5H_{10}O_5$, corresponding in many characteristics to the true glucoses and in others quite distinct from the latter, may be referred to collectively as *pentaglucoses*. This term expresses the relation between these compounds and the true, or hexaglucoses, and has already become established by some degree of use.[1]

The two bodies just mentioned are the only members of this group thus far observed. Of these, arabinose has been known for more than twenty years, but was regarded until within a short time as a true glucose; while xylose is a recent discovery,[2] and has also been shown by Tollens and his pupils to be a pentaglucose.[3]

The pentaglucoses are strictly sugar-like bodies, crystallinic, sweet, reducing Fehling's solution, and dextro-rotatory. In some respects, however, they differ decidedly from the true glucoses.

[1] Ber. d. chem. Ges. **21**, 2151, **22**, 1046, **23**, 137, **23**, 1751; Ann. Chem. (Liebig) **249**, 207, **254**, 304; This Journal **12**, 435, etc.

E. Fischer proposes a numerical nomenclature for the different series of sugars so notably extended by his syntheses, according to which this group are called the "*pentoses*." This is perhaps preferable to the term here used, and may find adoption eventually.

[2] Koch: Pharm. Ztschr. f. Russland **25**, 619, etc.

[3] Tollens and Mayer: Ber. d. chem. Ges. **21**, 647; Tollens and Wheeler: Ann. Chem. (Liebig) **254**, 304.

They are not subject to alcoholic fermentation, as has been previously proven for arabinose,[1] and as I am now able to announce for xylose. As a distinctive and specific reaction, the pentaglucoses produce large quantities of furfurol when subjected to the action of strong acids, and in this way are sharply separated from the true glucoses, which, under similar conditions, yield levulinic acid.[2] By perfected methods the amount of furfurol thus obtained amounts to nearly fifty per cent., when pure arabinose or xylose is used.[3]

The pentaglucoses have not been observed as occurring in nature, but are obtained by hydrolysis of certain plant constituents. These mother-substances are found either normally as a part of the cellular tissues of the plant, or in some notable examples as abnormal gum-like secretions. So far as is known the substances occurring under either of the above conditions are identical, although at the present time we have no means of distinguishing between those substances which will yield arabinose from those which will yield xylose.

Arabinose has been prepared from the cellular tissues of the sugar beet,[4] from gum arabic,[5] gum tragacanth,[6] cherry gum,[7] and from wheat bran.[8] Xylose has been obtained from woods of different species and jute,[9] and from straw.[10] From brewers' grains, *i. e.* from the outer seed-coats of barley, both arabinose and xylose have been prepared,[11] while from peach gum arabinose and galactose were obtained,[12] and gum arabic also would seem to contain the mother-substances of arabinose and galactose.

The nature of this substance, or these substances, from which the pentaglucoses are derived is not well understood. They are of a gummy nature and may be spoken of comprehensively as *gums*, a term clearly applicable in some cases but less so in others. In normal woody tissues, for instance, it is difficult to locate any material of the nature of gums, but by means of alkalies an amorphous substance may be extracted which is insoluble in water, alcohol, and ether, and which by the action of acids may be converted into one or the other of the pentaglucoses. This substance has been variously designated as metapectic acid, arabin,

[1] Ann. Chem. (Liebig) **249**, 257.
[2] Ber. d. chem. Ges. **21**, 2150; Ann. Chem. (Liebig) **249**, 227.
[3] Ber. d. chem. Ges. **23**, 1751. [4] Ibid. **1**, 58, 108. [5] Ibid. **6**, 612.
[6] Sachsse u. Martin: Phytochemische Untersuchungen. [7] Ibid.
[8] Ann. Chem. (Liebig) **249**, 239; also Ber. d. chem. Ges. **23**, 3110.
[9] Ann. Chem. (Liebig) **254**, 304. [10] Ber. d. chem. Ges. **23**, 137.
[11] Ann. Chem. (Liebig) **249**, 243. [12] This Journal **12**, 435.

wood gum, etc. Tollens and Allen have pointed out that the occurrence of this gummy material *in situ* corresponds closely to the lignin reaction with hydrochloric acid and phloroglucin.[1] Moreover, E. Schulze has lately shown that preparations of cellulose which, according to all appearances, were pure, still gave the lignin reaction and yielded an appreciable amount of furfurol,[2] indicating that these substances are most intimately connected with the ultimate cellular tissue, from which they are separated with difficulty. Wherever these gums occur they may be recognised by the furfurol reaction which characterises the pentaglucoses. In this reaction the pentaglucoses are doubtless formed as an intermediate product and themselves eventually yield furfurol. The furfurol test may therefore be applied to any crude material as a means of detecting the presence therein of these gums, which by proper treatment yield the pentaglucoses. Indeed, the search for and ultimate preparation of arabinose and xylose from several of the materials mentioned has been based upon the results of a preliminary furfurol test.

The continuation of my studies beyond this point, as described later, will perhaps increase the interest and importance attached to this group of bodies.

A.—*Occurrence of the Pentaglucoses.*

The reliability of the furfurol reaction as indicative of the presence of the pentaglucoses, or the gums from which they are derived, having been established, and having led to the preparation of arabinose and xylose from several unexpected sources, the question naturally followed: how frequently do these bodies occur in vegetable products, or how widely diffused may they be in nature? Strictly speaking, only the gums are found under these conditions; but since they are little known except in their derivatives the pentaglucoses, to which they seem to stand in direct relation, we may regard the former as representing the occurrence of the latter. If occurring commonly, they still find no recognition in our present analytical methods, toward which their reactions are those of the normal carbohydrates and glucoses. In the case of foods, results thus obtained may give rise to erroneous estimates of the values of certain materials, since we have no

[1] E. W. Allen: Inaugural Dissertation, Göttingen, 1890. [2] Ber. d. chem. Ges. **23**, 2579.

ground for assuming that the two classes are of equal or even similar nutritive value.

I have therefore examined a considerable variety of vegetable materials, including different parts and products of plants, for the purpose of detecting the presence of these gums as indicated by the production of furfurol when treated with strong acids. The list of materials might be greatly extended, but it suffices, perhaps, to show that these bodies are much more widely and abundantly distributed than is ordinarily supposed.

The method of making these tests is practically the same as that used in the original study of the reaction. It allows of a comparison of the amounts of furfurol produced from different sources under fairly constant conditions. The results, however, are not absolutely quantitative, failing to yield the highest possible amount of furfurol in comparison with the method proposed by Tollens and Günther.[1] Having commenced these studies, however, some time since, I have preferred to retain the original method, for the sake of comparison between earlier and later results. This method is as follows:

2–5 grams of the finely powdered, air-dried material are placed in a flask of 200–300 cc. capacity, with 50 cc. of sulphuric acid of 1.254 specific gravity. The flask is placed in a paraffin bath and connected with a condenser; through a second opening in the stopper connection is made with a reservoir from which water is allowed to drop into the flask with just sufficient rapidity to replace the loss by distillation and thus maintain a constant concentration of the acid. The bath is heated to 125° to 135° C. The first action of the acid is to convert the gums into pentaglucoses, followed at once by the decomposition of the latter, probably in this way,

$$C_5H_{10}O_5 = C_5H_4O_2 + 3H_2O.$$

The furfurol thus formed is distilled over and collected. This distillation is continued so long as there is evidence of the presence of furfurol in the distillate. This evidence is furnished by a reaction which is very delicate, and which consists in allowing a drop of the distillate to fall upon a strip of filter-paper moistened with aniline acetate. So sensitive is this reaction that one part of furfurol in one hundred thousand parts of water produces instantly

[1] Ber. d. chem. Ges. 23, 1751.

an intense red color upon the paper. In more concentrated solutions this color becomes darker and, eventually, reddish brown.

Usually eight to ten hours are required to complete the distillation, and the distillate amounts to 200–300 cc. The furfurol contained therein is next concentrated by fractional distillation to a volume of 3–6 cubic centimeters, in which it may in part appear in the form of light-yellow oily drops. Upon the addition of dilute ammonia a precipitate of furfuramide is formed, which is collected, dried over sulphuric acid, weighed, and the relation of its weight to that of the original material calculated in percentage. The following results therefore express the amount of *furfuramide* obtained from the various materials. But 1 gram of furfuramide theoretically requires for its production 1.6875 grams of a pentaglucose, and practically, under the conditions described, rather more. Hence the percentages given may be multiplied by the above factor (1.6785), and will then indicate *less than the actual amount* of pentaglucoses present. From about forty substances examined, the following thirty-one yielded appreciable amounts of furfuramide:

Hungarian grass,	3.34	per cent.	of furfuramide.
Timothy hay,	1.18	"	"
Corn stover, I,	2.89	"	"
" " II,	1.48	"	"
Maize ensilage,	0.91	"	"
Clover hay,	1.55	"	"
Clover ensilage,	0.40	"	"
Wheat straw,	4.16	"	"
Oat straw,	2.29	"	"
Malt sprouts,	1.82	"	"
Brewers' grains,	7.20	"	"
Corn bran, I,	0.84	"	"
" " II,	1.80	"	"
Linseed meal,	1.20	"	"
Corn and cob meal,	0.59	"	"
Corn cobs,	8.16	"	"
Oatmeal,	0.40	"	"
Beet pulp,	3.59	"	"
Cotton-seed hulls,	3.66	"	"
Pulp of strawberries,	1.95	"	"
Dung of cattle fed on maize ensilage,	2.88	"	"

Dung of cattle fed on corn stover,	3.94	per cent of furfuramide.
Gum arabic,	5.46	" "
Cherry gum,	8.14	" "
Gum tragacanth,	8.08	" "
Peach gum,	4.84	" "
White lupine seeds,	0.95	" "
Yellow " "	1.69	" "
Coats of orange seeds,	1.85	" "
Orange peel,	0.69	" "
Watermelon seeds,	2.70	" "

The following materials yielded no perceptible quantities of furfuramide, but all gave strong qualitative reactions for furfurol, and it is hardly too much to expect that with a better method of distillation these also might yield furfurol in noticeable amounts:

Dried strawberries,
Cotton-seed cake,
Corn meal,
Dried sweet potato,
Kernels of orange seeds,
Raw coffee,
Buckwheat,
Beans.

Under the stated conditions these results, indicating that, in more than three-fourths of these materials, taken at random, there exist the equivalents of from 1 to 12, or more, per cent. of pentaglucoses, plainly prove the common and abundant occurrence of the latter. It is evident, therefore, that among the vegetable products usually classed as carbohydrates the pentaglucoses, or the gums giving rise to them, play an important part.

B.—*Quantitative Reduction of Fehling's Solution by the Pentaglucoses.*

Both arabinose and xylose reduce Fehling's solution strongly, but their quantitative relation to it has not previously been studied, with the exception of a brief mention by Bauer of some limited determinations for arabinose, from which he concluded that it possessed in a slight degree greater reducing power than dextrose.[1]

[1] Landwirthschaftliche Versuch-Stationen **36**, 304.

In view of the common occurrence of the pentaglucoses, as already pointed out, it is evident that in the quantitative examination of any material for carbohydrates by hydrolytic methods, *i. e.* by inversion with acids and titration of the glucose thus formed with Fehling's solution, we may be dealing not only with the true glucoses derived from starch, cane sugar, etc., but also with more or less of one or both of the pentaglucoses, since we know that the gums from which the latter are derived easily undergo hydrolytic change by the action of acids. Such analytical results may, therefore, be erroneous from two causes: first, from the assumption that the reduction of Fehling's solution is due solely to the presence of the true glucoses; or, second, from the assumption that the pentaglucoses, when present, reduce Fehling's solution in the same degree as the true glucoses.

Take, for example, such a material as brewers' grains, in which it might be desired to ascertain the thoroughness of malting and fermentation by determining the residual carbohydrates. Such material might contain no trace of starch or sugar and yet might give abundant indications of the presence of these substances after inversion, because it contains so large an amount of the pentaglucose bodies that it is possible to isolate from it 2 per cent., or more, of the crystallised pentaglucoses.[1]

It seemed important, therefore, to know the relations existing between these bodies and the true glucoses, and I have therefore determined the comparative values of arabinose and dextrose in dilute solutions toward Fehling's solution.

1. *Arabinose.*—The material used was prepared by me from cherry gum, and was pure, as was shown by its specific rotation ($[\alpha]_D = 104.1°$). From this material, solutions of 1, ¾, ½ and ¼ per cent. strength were made. The Fehling's solution was prepared according to the standard formula, viz. 34.639 grams of hydrous copper sulphate dissolved to a volume of 500 cc., and 60 grams sodium hydrate with 173 grams sodium-potassium tartrate dissolved to a volume of 500 cc., the two solutions being preserved separately, and mixed in equal volumes just before using. The determinations were made gravimetrically, as follows:

70 cc. of the Fehling's solution were brought to boiling, and exactly 25 cc. of the arabinose solution quickly run in from a full pipette, after which the whole was kept over the flame exactly four

[1] Ann. Chem. (Liebig) **249**, 241.

minutes, of which the first fifty to sixty seconds were consumed in bringing the liquid to boiling again. The time of boiling and filtering was observed carefully. The precipitated cuprous oxide was collected on a Soxhlet asbestos filter with the aid of a pump, washed with boiling water, alcohol and ether, reduced to metallic copper in a current of dry hydrogen over a low flame, and, after cooling in hydrogen, weighed. The following are the results obtained:

1-*per cent. solution.*—25 cc., containing 0.250 gram arabinose, precipitated respectively:

1. 0.4850 gram copper.
2. 0.4874 " "
3. 0.4860 " "

An average of 0.48623 gram copper, or for 0.001 gram arabinose 0.001945 gram copper.

¾-*per cent. solution.*—25 cc., containing 0.1875 gram arabinose, precipitated respectively:

1. 0.3621 gram copper.
2. 0.3631 " "
3. 0.3604 " "

An average of 0.36187 gram copper, or for 0.001 gram arabinose 0.001929 gram copper.

½-*per cent. solution.*—25 cc., containing 0.125 gram arabinose, precipitated respectively:

1. 0.2446 gram copper.
2. 0.2430 " "
3. 0.2479 " "

An average of 0.2448 gram copper, or for 0.001 gram arabinose 0.001958 gram copper.

¼-*per cent. solution.*—25 cc., containing 0.0625 gram of arabinose, precipitated respectively:

1. 0.1264 gram copper.
2. 0.1248 " "
3. 0.1250 " "

An average of 0.1254 gram copper, or for 0.001 gram arabinose 0.002 gram copper.

From this it appears that in solutions of 1 per cent., or less, strength, 1 milligram of arabinose precipitates 1.9–2 milligrams of copper.

2. *Xylose.*—The material used was prepared from wheat straw, and was of the desired purity, as shown by its specific rotation ($[\alpha]_D = 18.41°$).[1] The determinations were made under conditions as nearly as possible identical with those for arabinose, with the following results:

1-*per cent. solution.*—25 cc., containing 0.250 gram xylose, precipitated respectively:

1. 0.4686 gram copper.
2. 0.4640 " "
3. 0.4667 " "

An average of 0.4664 gram copper, or for 0.001 gram xylose 0.001864 gram copper.

¾-*per cent. solution.*—25 cc., containing 0.1875 gram xylose, precipitated respectively:

1. 0.3444 gram copper.
2. 0.3446 " "
3. 0.3462 " "

An average of 0.3451 gram copper, or for 0.001 gram xylose 0.001841 gram copper.

½-*per cent solution.*—25 cc., containing 0.125 gram xylose, precipitated respectively:

1. 0.2378 gram copper.
2. 0.2366 " "
3. 0.2381 " "

An average of 0.2375 gram copper, or for 0.001 gram xylose 0.0019 gram copper.

¼-*per cent. solution.*—25 cc., containing 0.0625 gram xylose, precipitated respectively:

1. 0.1235 gram copper.
2. 0.1222 " "
3. 0.1217 " "

An average of 0.1224 gram copper, or for 0.001 gram xylose 0.001959 gram copper.

Under the stated conditions, therefore, 1 milligram of xylose precipitates 1.86–1.959 milligrams of copper.

Dextrose, the most strongly reducing glucose heretofore

[1] This unusually fine preparation was kindly furnished me by Dr. E. W. Allen, of Washington, D. C., who prepared it himself, and to whom my thanks are due.

studied, precipitates, under similar conditions, 1.8–1.9 milligrams copper, or slightly less than the pentaglucoses. Stated in another way, the amounts of the different sugars in 1-per cent. solution required to precipitate the entire copper from 1 cc. of Fehling's solution are:

Arabinose, ...	.004523 gram.[1]
Xylose, ...	.004617 "
Dextrose, ...	.004753 "
Levulose, ...	.005144 "
Invert sugar, ...	.004941 "
Galactose, ...	.005110 "
Milk sugar, ...	.006757 "
Maltose, ...	.007780 "

From this it appears that the two pentaglucoses are the most strongly reducing sugars yet studied, and this is particularly true of arabinose. Both differ from the value for invert sugar sufficiently seriously to affect the accuracy of analyses in which they are concerned but not recognised.[2]

C.—*Fermentability of the Pentaglucoses.*

In connection with the history of arabinose, mention is made by various investigators of its behavior toward fermenting agents, in which it is regarded as not subject to alcoholic fermentation. In some earlier studies of this body by Prof. Tollens and myself this view was substantiated, and it was further shown that this was a specific property of arabinose, in contradistinction from the true glucoses, galactose, levulose and dextrose, which are all fermentable, some conflicting views regarding galactose being at that time cleared up.[3]

In his original paper, in which the discovery of xylose was announced, Koch described the same as non-fermentable, which was somewhat remarkable if it were a true glucose, as was at that time supposed. Its identity as a pentaglucose being afterwards established, it was of importance to show that it is, like arabinose, strictly non-fermentable, thus fixing this as a character of the

[1] Tollens: Handbuch der Kohlenhydrate, p. 284.

[2] H. Ost (Ber. d. chem. Ges. **23**, 3006) notes the reducing effect of arabinose on a solution of potassium-copper carbonate, and finds its value lower than that of dextrose, but higher than that of galactose, toward this reagent.

[3] Ann. Chem. (Liebig) **249**, 257; and Ber. d. chem. Ges. **21**, 1572.

$C_5H_{10}O_5$ group. In order to determine the non-fermentability of a given substance it is very essential that such a fermentation-test shall be made under conditions favorable to the requirements and activity of the yeast-plant used. No better example of this is known than that of galactose, which has been reported non-fermentable by some experimenters, who seemed to have worked with poorly nourished yeast or that deficient in vitality. Where there has been due regard for these conditions, galactose will produce nearly theoretical results of fermentation, although it is plain that it is less rapidly and easily subject to the influence of yeast than its isomers, levulose and dextrose. The method used for xylose was the same as that formerly applied to arabinose. Its special feature consists in supplying the yeast used with a nutrient extract, made by boiling 100 cc. of the semi-fluid brewery yeast with 100 cc. of water and filtering off the dark-brown extract resulting. Such a solution contains the natural constituents of the yeast, and, as a nutrient, seems to give better results than artificially prepared solutions of salts.

In the study of xylose two sets of experiments were performed. In one the carbon dioxide produced was collected, and in the other the alcohol. The former were conducted in eudiometer tubes which were first filled to within 15 cc. of their capacity with mercury; then were added 5 cc. of distilled water, 5 cc. of the above-described nutrient solution, 5 cc. of a mixture of 5 grams of Fleischmann's compressed yeast with 50 cc. of water, and, lastly, the weighed xylose. The tube was then inverted in a mercury trough, and the gaseous products of fermentation were allowed to collect in the upper end. A second tube filled in exactly the same way, but containing cane sugar instead of xylose, was arranged for comparison and as an index of the activity of the yeast.

For the first experiment were taken 0.139 gram xylose and 0.1566 gram cane sugar. Within a quarter of an hour lively fermentation had begun in the cane-sugar solution, and after ten hours seemed practically complete. In the xylose solution no action was observed. After six days, no farther action being noticeable, the necessary readings were taken for calculating the amount of gas collected (including that absorbed by the liquid) from the cane sugar. Less than 0.5 cc. of gas had collected on the xylose solution, too little to indicate any appreciable fermentative

action. The gas produced from the cane sugar was wholly absorbed by potassium hydrate solution, and was therefore carbon dioxide. Reducing the temperature and pressure to 0° and 760 mm., the volume of the undissolved gas from cane sugar was 31.07 cc., and of that absorbed in the solution, 13.16 cc., or a total of 44.23 cc., equal to 78.7736 milligrams, or 50.49 per cent. of the sugar used.

In the second experiment were taken 0.1526 gram of cane sugar and 0.1572 gram xylose under the same conditions as before. In this case also the cane sugar underwent active fermentation, but no action was observed in the xylose solution. After seven days, measurements of the gas from the cane sugar, which was found to be carbon dioxide, gave a total of 78.506 milligrams, or 51.5 per cent.

The yield of alcohol was next determined in a third experiment. 1 gram each of xylose and cane sugar was placed in flasks of about 200 cc. capacity, with 35 cc. of water, 5 cc. of the nutrient fluid and 10 cc. of the yeast mixture. The flasks were closed with a water-valve. As in the other cases, the cane sugar showed active fermentation, but no action was detected in the xylose. After five days both solutions were neutralised with sodium carbonate, and after slight dilution, 50 cc. distilled off and the alcohol determined in the distillates by taking their specific gravities with a Sprengel's specific-gravity flask.

50 cc. of distillate from the cane-sugar solution had the specific gravity 0.9982, equal to 0.472 gram alcohol, or 47.2 per cent.

50 cc. of distillate from the xylose solution had the specific gravity 0.9999, showing no appreciable amount of alcohol present.

Summing up the results of these experiments, we have:

		Carbon-dioxide.	Alcohol.
1.	Xylose,	...	...
	Cane sugar,	50.49 per cent.	...
2.	Xylose,	...	...
	Cane sugar,	51.50 "	...
3.	Xylose,	...	...
	Cane sugar,	...	47.20 per cent.
Calculated for $C_{12}H_{22}O_{11}$,		51.46 "	48.54 "

From this it appears that under those conditions which produced almost theoretical fermentation of cane sugar, xylose did not ferment in the least. It is therefore, like its isomer arab-

inose, non-fermentable, and this becomes a specific characteristic of the pentaglucoses.

It seems, therefore, that the pentaglucoses are of abundant occurrence in nature in the form of gum-like constituents of vegetable tissues; that these bodies are easily converted into the pentaglucoses themselves, and in such form are liable to be confused with the true glucoses, from which, however, they have quite different analytical, and as far as we know, economic values. In addition to the furfurol reaction, non-fermentability seems to be a further distinguishing property of the pentaglucoses.

In view of the importance of this group, a method by which they may be determined quantitatively in the presence of the true glucoses seems desirable. Such a method has lately been proposed by Günther and Tollens.[1] Simultaneously with them I have been engaged upon the same subject with somewhat similar results, a more extended report of which is for the present reserved.

ON THE ACTION OF AMMONIA AND ALKYLAMINES ON ETHYLIC ACETOSUCCINATE AND SUBSTITUTED ETHYLIC ACETOSUCCINATES.

By William Orren Emery.

The following research was undertaken for the purpose of finding, if possible, a general method by which unsaturated γ-lactams might be prepared, and, at the same time, of affording further proofs of the constitution of the products formed by the action of ammonia and alkylamines on compounds analogous to ethylic acetoacetate. Although the investigation has by no means been brought to an end, still it was thought expedient to offer the results thus far obtained.

The action of ammonia and alkylamines on ethylic acetoacetate has been, for many chemists, a fruitful field for experiment. The facts gathered by Collie[2] with regard to the action of ammonia on ethylic acetoacetate were insufficient to determine the constitution of the product formed by this reaction. One had the choice between the two formulæ:

[1] Ber. d. chem. Ges. **23**, 1751. [2] Ann. Chem. (Liebig) **226**, 294.

$$\text{I.}\quad \begin{matrix} CH_3.C.CH_2.CO_2R \\ \| \\ NH \end{matrix}\text{, ethylic } \beta\text{-imidobutyrate.}$$

$$\text{II.}\quad \begin{matrix} CH_3.C=CH.CO_2R \\ | \\ NH_2 \end{matrix}\text{, ethylic } \beta\text{-amidocrotonate.}$$

Not until Kuckert[1] had, by the action of methylamine and diethylamine on ethylic acetoacetate, succeeded in preparing the compounds

$$\begin{matrix} CH_3.C=CH.CO_2R \\ | \\ NH.CH_3 \end{matrix}\text{, ethylic } \beta\text{-methylamidocrotonate, and}$$

$$\begin{matrix} CH_3.C=CH.CO_2R \\ | \\ N(C_2H_5)_2 \end{matrix}\text{, ethylic } \beta\text{-diethylamidocrotonate;}$$

and, further, not until Conrad and Epstein[2] had observed that, by the action of ammonia on ethylic acetodiethylacetate, $CH_3.CO.C(C_2H_5)_2.CO_2R$, as well as on ethylic acetodichloracetate, $CH_3.CO.CCl_2.CO_2R$, no amido-derivative resulted; did it become evident that only formula II could be the correct one. There can, therefore, be no question that ammonia and alkylamines act in the same way on ethylic acetoacetate. The resulting products of this reaction must be regarded as derivatives of ethylic α-crotonate, $CH_3.CH=CH.CO_2R$.

In the case of ethylic acetoacetate we have an example of an ether of a β-ketonic acid which, as we have seen, forms with ammonia ethylic β-amidocrotonate. It has been, thus far, impossible to bring about in this latter compound an intermolecular condensation. If we now turn our attention to an ether of a γ-ketonic acid, we shall find that ethylic acetopropionate, $CH_3.CO.CH_2.CH_2.CO_2R$, is the simplest example of this kind. The behavior of this ether towards ammonia has already been investigated by Wolff,[3] who found the resulting product of this reaction to be the so-called acetopropionamide, which, according to Wolff, has the constitution represented by the formula $CH_3.CO.CH_2.CH_2.CO.NH_2$. This amide does not appear capable of undergoing condensation.

If we now consider for a moment the ether of a dibasic ketonic acid—for example, ethylic acetosuccinate, $\begin{matrix} CH_3.CO.CH.CO_2R \\ | \\ CH_2.CO_2R \end{matrix}$—

[1] Ber. d. chem. Ges. **18**, 618. [2] Ibid. **20**, 3056. [3] Ann. Chem. (Liebig) **229**, 262.

we have at once the ether of a β- and a γ-ketonic acid. Conrad and Epstein[1] have already made a short study of the action of ammonia on ethylic acetosuccinate, and have succeeded in preparing the so-called ethylic amidoacetosuccinate,

$$\begin{array}{l} CH_3.C = C.CO_2R \\ \quad\quad\quad\quad | \quad\quad | \\ \quad\quad\quad NH_2 \; CH_2.CO_2R \end{array}.$$

It will be readily seen from the formula above that the amido-rest occupies the β-position to the one carboxyl-group, the γ-position to the other. If under favorable conditions it were possible to split off the elements of alcohol from this compound, the most reasonable supposition would be that the condensation would take place between the amido-rest and that carboxyl-group occupying the γ-position to it. Experiment has shown that the condensation does indeed result in the manner indicated. The product formed by the action of ammonia on ethylic acetosuccinate loses alcohol quite readily, and is thereby changed to the compound

having the constitutional formula

$$\begin{array}{l} CH_3.C = C.CO_2R \\ \quad\quad\quad\quad | \quad\quad | \\ \quad\quad\quad NH \quad CH_2 \\ \quad\quad\quad\quad \diagdown / \\ \quad\quad\quad\quad CO \end{array}$$

Similar results were obtained by Weltner,[2] who investigated the action of ammonia in the heat on ethylic acetophenylsuccinate, $\begin{array}{l} CH_3.CO.CH.CO_2R \\ \quad\quad\quad\quad | \\ C_6H_5.CH.CO_2R \end{array}$, and found that, among other things, a substance was formed which must have one of the two following formulæ:

Lactam.

$$\begin{array}{l} CH_3.C = C.CO.NH_2 \\ \quad\quad\quad | \quad\quad | \\ \quad\quad NH \quad CH.C_6H_5 \\ \quad\quad\quad \diagdown / \\ \quad\quad\quad CO \end{array}$$

Lactim.

$$\begin{array}{l} CH_3.C = C.CO.NH_2 \\ \quad\quad\quad | \quad\quad | \\ \quad\quad\quad N \quad CH.C_6H_5 \\ \quad\quad\quad \diagdown\!\!\diagup \\ \quad\quad\quad C.OH \end{array}$$

Weltner was unable to decide from his experiments which of the two formulæ was the correct one.

From the above the question naturally arises: (*a*) Is it possible to generalise this reaction? and (*b*) is it possible to furnish conclusive proof which shall establish with certainty the lactam or the lactim formula?

[1] Ber. d. chem. Ges. **20**, 3058. [2] Ibid. **18**, 793.

In an endeavor to bring about a solution of these problems I have carried out the following series of experiments:

I. Ammonia and ethylic acetosuccinate.
II. Methylamine and ethylic acetosuccinate.
III. Ethylamine " " "
IV. Propylamine " " "
V. Isobutylamine " " "
VI. Amylamine " " "
VII. Ammonia " " acetomethylsuccinate.
VIII. Ammonia " " acetophenylsuccinate.

In every case in which ammonia was used it was employed in the form of an alcoholic solution saturated at 0°. An aqueous solution of ammonia was discarded for the reason that its saponifying action on carbethoxyl-rests would be greater than that of the alcohol solution, and such an action I desired if possible to avoid. As my chief object in this research was an examination of the end-products which arise by the action of ammonia and alkylamines on the above-mentioned ketonic ethers, I have in general paid but little attention to the intermediate products formed by this reaction.

I.—*Ammonia and Ethylic Acetosuccinate.*[1]

Ammonia and ethylic acetosuccinate unite readily in alcoholic solution. The reaction may be conveniently performed as follows: One volume of ethylic acetosuccinate is gradually mixed with two volumes of a solution of ammonia in absolute alcohol saturated at 0°. The mixture is kept in a small well-corked flask and allowed to stand 24 hours in a cool place, after which it is poured into a shallow dish in order that it may evaporate slowly at the ordinary temperature. In about 24 hours the contents of the evaporating dish have become a mass of large transparent crystals. These are first freed from the small amount of mother-liquor which accompanies them, by spreading on porous plates, and are then recrystallised once or twice from warm ethyl acetate.

[1] In preparing the ethylic acetosuccinate used in the following experiments from ethylic sodiumacetoacetate, I have found it more expedient to employ bromacetic ether in place of the more common chlorine-compound, from the fact that the former is more readily acted upon by ethylic sodiumacetoacetate than chloracetic ether, and the result is a far better yield of ethylic acetosuccinate. Great care must, however, be taken to cool well on bringing together the alcoholic solution of ethylic sodiumacetoacetate and bromacetic ether, since the reaction takes place almost instantly, and, indeed, with the evolution of much heat. Bromacetic acid may be conveniently made according to the method of Michael (this Journal 5, 202).

Large, transparent, highly refractive crystals were obtained which melt at 62°.[1] The analysis gave the following results:

I. 0.2007 gram substance gave 0.4120 gram CO_2 and 0.1478 gram H_2O.[2]

II. 0.1311 gram substance gave 0.2686 gram CO_2 and 0.0932 gram H_2O.

III. 0.2805 gram substance gave the following data: $B = 746$, $t = 13°$, $v = 15.8$ cc.

	Calculated for $C_{10}H_{17}NO_4$.	Found. I.	II.	III.
C	55.81	55.98	55.88	...
H	7.91	8.18	7.90	...
N	6.51	...	...	6.53
O	29.77	...	...	...

For reasons which will be discussed further on, I would propose the name "α-amidoethylidenesuccinic ether" for the compound obtained by the action of ammonia on ethylic acetosuccinate. Its formation evidently takes place in two phases perfectly analogous to the formation of β-amidocrotonic ether, and may be represented by the equations:

$$\begin{array}{l} CH_3.CO.CH.CO_2R \\ \qquad\quad | \\ \qquad CH_2.CO_2R \end{array} + \begin{array}{l} H \\ | \\ NH_2 \end{array} = \begin{array}{l} CH_2.C(OH).CH.CO_2R \\ \qquad\quad | \qquad\quad | \\ \qquad NH_2 \qquad CH_2.CO_2R \end{array}, \text{ and}$$

$$\begin{array}{l} CH_3.C(OH).C(H).CO_2R \\ \qquad\quad | \qquad\quad | \\ \qquad NH_2 \qquad CH_2.CO_2R \end{array} = \begin{array}{l} CH_2.C=C.CO_2R \\ \qquad\quad | \quad | \\ \qquad NH_2 \quad CH_2.CO_2R \end{array} + H_2O.$$

α-Amidoethylidenesuccinic ether is readily soluble in alcohol, ether and chloroform, less so in ethyl acetate and carbon bisulphide, and insoluble in cold water. On heating with acetic anhydride in slight excess for several hours at 155°–160°, an acetyl derivative was formed. The product was purified by washing first with water, then with a dilute solution of sodium carbonate, after which it was taken up with ether, the ethereal solution dried over calcium chloride, and the ether finally evaporated in a vacuum desiccator. In this way a thick, bright straw-colored oil was obtained which on analysis gave the following figures:

I. 0.1507 gram substance gave 0.3115 gram CO_2 and 0.1018 gram H_2O.

[1] Conrad u. Epstein: Ber. d. chem. Ges. **20**, 3058.

[2] All the combustions were performed in a tube open at both ends.

II. 0.2266 gram substance gave 0.4664 gram CO_2 and 0.1513 gram H_2O.

III. 0.3075 gram substance gave the following data: $B = 744.5$, $t = 13°$, $v = 14.5$ cc.

IV. 0.2161 gram substance gave 0.4446 gram CO_2 and 0.1458 gram H_2O.[1]

	Calculated for $C_{12}H_{19}NO_5$.	Found. I.	II.	III.	IV.
C	56.03	56.37	56.13	...	56.11
H	7.39	7.50	7.42	...	7.49
N	5.45	...	...	5.52	...
O	31.13	...	...	...	...

This substance, for which I propose the name "α-acetylamidoethylidenesuccinic ether," is formed in a way exactly analogous to that of β-acetylamidocrotonic ether[2] from β-amidocrotonic ether, according to the equation:

$$\begin{array}{l} CH_3.C = C - CO_2R \\ \quad\quad\;\; | \quad\quad | \\ \quad\quad NH_2 \quad CH_2.CO_2R \end{array} + \begin{array}{l} CH_3.CO \\ CH_3.CO \end{array} > O =$$

$$\begin{array}{l} CH_3 - C = C - CO_2R \\ \quad\quad\quad\;\; | \quad\quad | \\ CH_3.CO.NH \; CH_2.CO_2R \end{array} + CH_3.CO.OH.$$

The new compound may be distilled under greatly diminished pressure without decomposition. Under a pressure of about 11 mm. the boiling point is 175°–176° (temperature of paraffin-bath 195°). The specific gravity was found to be

$$d\,\frac{20}{4} = 1.12873.$$

The behavior of α-amidoethylidenesuccinic ether on heating is of great interest, as showing its capability of being changed into a lactam of the formula $C_8H_{11}NO_3$. The operation may be conveniently performed as follows: The amido ether is heated in a paraffin-bath at 145°–150° until the vapors of alcohol cease to be given off. On cooling the product becomes a viscous mass, and generally shows but little inclination to crystallise. It is now dissolved in warm ether and the latter allowed to evaporate in a

[1] Combustion IV was made from the substance after it had been distilled.

[2] Collie: Ann. Chem. (Liebig) **226**, 309. I wish to take this opportunity of pointing out the probable identity of β-acetylamidocrotonic ether with the so-called β-acetylamidobutyric ether, which Canzoneri and Spica (Gazz. chim. ital. **14**, 491) obtained by the action of acetamide on ethylic acetoacetate. Beilstein evidently regards these two substances as different, as he gives them twice in his hand-book, 2d edition, I, 542, 543.

vacuum desiccator. The crystals, consisting of needles, are freed from the mother-liquor by drying on porous plates, and are then purified by repeated crystallisation from warm ether. After one or two recrystallisations, fine snow-white needles are obtained which melt at 133°–134°. The same substance is formed when *a*-amidoethylidenesuccinic ether is distilled under greatly diminished pressure. By rapid distillation the greater part of the *a*-amidoethylidenesuccinic ether passes over unchanged; if, on the other hand, the distillation be allowed to take place slowly, a portion goes over unchanged, while another loses alcohol and distils as a thick colorless oil which gradually solidifies to snow-white needles. The boiling point was observed to be 195° (temperature of the paraffin-bath 215°–220°) under a pressure of about 12 mm. The lactam, if prepared in this way, needs only one recrystallisation from warm ether in order to be brought into a state of absolute purity. Analysis gave the following figures:

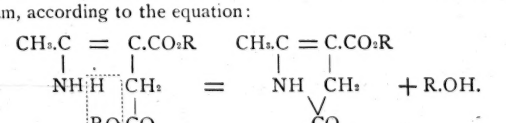
I. 0.1361 gram substance gave 0.2841 gram CO_2 and 0.0830 gram H_2O.

II. 0.1313 gram substance gave 0.2744 gram CO_2 and 0.0782 gram H_2O.

III. 0.2017 gram substance gave the following data: $B=746$, $t=13°$, $v=14.5$ cc.

	Calculated for $C_8H_{11}NO_3$.	I.	Found. II.	III.
C	56.80	56.93	56.99	...
H	6.51	6.77	6.62	...
N	8.28	...	...	8.33
O	28.40	...	...	...

a-Amidoethylidenesuccinic ether is therefore converted into its lactam, according to the equation:



The new substance is easily soluble in alcohol, more sparingly in ether and carbon bisulphide, and may be recrystallised from water. If it be treated with a solution of sodic ethylate in perfectly dry alcohol-ether, a white insoluble sodic compound is formed which very soon deliquesces when exposed to the air.

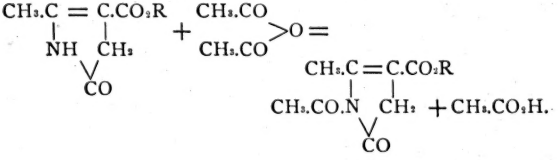
Bromine gives in a solution of carbon bisulphide a crystalline product, which has not yet been further examined. If the lactam be heated a few hours at 155°–160° in a sealed tube with an excess of acetic anhydride, a small quantity of an acetyl compound is formed. This gradually separates in the form of a sandy powder from the brown-colored liquid obtained by heating, and may be conveniently freed from the mother-liquor by drying on a porous plate. After one recrystallisation from ether it was obtained as a white powder, melting at 141°–142°, and on analysis gave the following figures:

I. 0.1882 gram substance gave the following data: $B=750$, $t=15°$, $v=10.9$ cc.

II. 0.1509 gram substance gave the following data: $B=752$, $t=19°$, $v=9$ cc.

	Calculated for $C_{10}H_{13}NO_4$.	Found. I.	II.
C	56.87	...	...
H	6.16	...	...
N	6.64	6.69	6.78
O	30.33	...	...

The acetyl compound has therefore the formula $C_{10}H_{13}NO_4$. It is produced from the lactam of *a*-amidoethylidenesuccinic ether and acetic anhydride, according to the equation



II.—*Methylamine and Ethylic Acetosuccinate.*

So far as the yield of lactam by the action of alkylamines on ethylic acetosuccinate is concerned, these bases may be used either in the pure state or in the form of an absolute-alcoholic solution. In every case the substances unite readily, while the yield of lactam approaches very nearly that of the theory. From the investigations of Collie [1] and of Kuckert,[2] it appears extremely probable that the former observed the formation of the first

[1] Ann. Chem. (Liebig) **226**, 298. [2] Ber. d. chem. Ges. **18**, 618.

product arising from the action of ammonia on ethylic acetoacetate,

$$CH_3.CO.CH_2.CO_2R + NH_3 = CH_3.\underset{\displaystyle NH_2}{C(OH)}.CH_2.CO_2R \quad ;$$

and the latter the formation of the first product formed by the action of methylamine on ethylic acetoacetate,

$$CH_3.CO.CH_2.CO_2R + CH_3.NH_2 = CH_3.\underset{\displaystyle NH.CH_3}{C(OH)}.CH_2.CO_2R \quad .$$

Owing, however, to the great instability of these compounds it was found impossible to analyse them. Although, by the action of alkylamines on ethylic acetosuccinate, I have in no case been able to isolate the intermediate products, still I believe the reaction takes place in a perfectly analogous way, and may be represented by the following general equations:

I. $$CH_3.CO.\underset{\displaystyle CH_2.CO_2R}{CH}.CO_2R + R.NH_2 = CH_3.\underset{\displaystyle R.NH}{C(OH)}.\underset{\displaystyle CH_2.CO_2R}{CH}.CO_2R \quad .$$

II. $$CH_3.\underset{\displaystyle R.NH}{C(OH)}\underset{\displaystyle CH_2.CO_2R}{CH}.CO_2R = CH_3.\underset{\displaystyle R.NH}{C}=\underset{\displaystyle CH_2.CO_2R}{C}.CO_2R + H_2O.$$

III. $$CH_3.\underset{\displaystyle RO}{C}=\underset{\displaystyle CO}{C}.CO_2R \quad \underset{\displaystyle R.N}{CH_3}=\underset{\displaystyle CO}{CH_2} + R.OH.$$

In order to prepare the methylamine derivative of ethylic acetosuccinate I operated as follows: ethylic acetosuccinate was dissolved in twice the volume of absolute alcohol, and this solution saturated with somewhat more than the calculated amount of methylamine. This mixture, after being kept in a cool place for 24 hours, was then allowed to evaporate in an open dish at the ordinary temperature. However, as the product showed no tendency to crystallise, it was then fractioned under greatly diminished pressure. After alcohol and water had passed over, a thick, colorless oil was obtained which, under a pressure of about 11 mm., boiled constantly at 160° (temperature of paraffin-bath 185°), and gradually solidified to a very compact mass of snow-white crystals. The latter, upon recrystallisation from ether or carbon bisulphide, showed the melting point 42°, and gave the following figures on analysis:

I. 0.2005 gram substance gave 0.4349 gram CO_2 and 0.1311 gram H_2O.

II. 0.1738 gram substance gave 0.3762 gram CO_2 and 0.1134 H_2O.

III. 0.2234 gram substance gave the following data: $B = 749.5$, $t = 11.5°$, $v = 14.8$ cc.

	Calculated for $C_9H_{13}NO_3$.	Found. I.	II.	III.
C	59.02	59.23	59.06	...
H	7.10	7.26	7.25	...
N	7.65	...	...	7.70
O	26.23	...	...	...

The new substance is extremely soluble in ether and carbon bisulphide, in contrast to the lactam of *a*-amidoethylidenesuccinic ether. On heating with acetic anhydride I was unable to obtain an acetyl derivative.

III.—*Ethylamine and Ethylic Acetosuccinate.*

Ethylic acetosuccinate and ethylamine were mixed in equal molecular proportions, and to this mixture twice the volume of absolute alcohol was added. After standing about 24 hours in the cold, the yellow-colored product was fractioned under diminished pressure. When alcohol and water had been removed, a fraction was obtained which, under a pressure of about 14 mm., boiled constantly at 165° (temperature of paraffin-bath 190°). On cooling the distillate slowly solidified to a snow-white mass of very fine needles, which, after one recrystallisation from carbon bisulphide, melted at 75°–76°, and on analysis gave the following figures:

I. 0.1510 gram substance gave 0.3352 gram CO_2 and 0.1051 gram H_2O.

II. 0.1532 gram substance gave 0.3390 gram CO_2 and 0.1061 gram H_2O.

III. 0.2102 gram substance gave the following data: $B = 759$, $t = 19°$, $v = 13.2$ cc.

IV. 0.1836 gram substance gave the following data: $B = 757.5$, $t = 20°$, $v = 12$ cc.

	Calculated for $C_{10}H_{15}NO_3$.	Found. I.	II.	III.	IV.
C	60.91	60.54	60.35	...	...
H	7.61	7.73	7.69	...	...
N	7.11	...	...	7.21	7.45
O	24.37	...	...	...	...

This new substance, which is the lactam of *α*-ethylamidoethylidenesuccinic ether, is formed according to the following equation:

$$\begin{array}{l} CH_3.C=C.CO_2R \\ \quad\quad | \quad\quad | \\ C_2H_5.N\boxed{H}\boxed{CH_2.CO}\boxed{OR} \end{array} = \begin{array}{l} CH_2.C=C.CO_2R \\ \quad\quad | \quad\quad | \\ C_2H_5.N \quad CH_2 \\ \quad\quad\quad \vee \\ \quad\quad\quad CO \end{array} + R.OH.$$

It is very similar in character to the preceding compound. In an attempt to regenerate the ether of which it is the lactam, by heating a short time with absolute alcohol, it was found that by far the greater part, if not all, had remained unchanged; for on evaporating the alcohol in a vacuum, colorless needles melting at 75°–76° were obtained. A nitrogen determination led to the formula $C_{10}H_{15}NO_3$. Further, it was found that the lactam is formed in part in the alcoholic solution of ethylamine and ethylic acetosuccinate. For example, such a solution, after remaining three days in the cold, was freed from alcohol and water in a vacuum, without the application of external heat. The residual liquid solidified in the form of a mass of needles. These, after being dried on a porous plate and recrystallised from carbon bisulphide, melted at 75°–76° and gave values which led to the formula $C_{10}H_{15}NO_3$. Combustion IV was made with the substance obtained in this way. The easy formation of the lactam, as above described, is quite remarkable, both in showing the great tendency of *α*-ethylamidoethylidenesuccinic ether to go over into its lactam, and in explaining the unusual stability of the latter compound upon being heated with alcohol.

IV.—*Propylamine and Ethylic Acetosuccinate.*

These two substances unite with great readiness when mixed either in the pure state or in alcoholic solution. I have generally operated without the aid of alcohol. The mixture, on standing 24 hours, was found to have become cloudy, owing to the separation of water. This was separated mechanically from the remaining liquid and the latter purified by fractional distillation. The greater portion boiled constantly, under a pressure of about 14–15 mm., at 172° (temperature of paraffin-bath 188°), and upon cooling solidified to a compact mass of snow-white needles. These, after one recrystallisation from carbon bisulphide, melted at 50° and gave the following figures on analysis:

I. 0.1500 gram substance gave 0.3434 gram CO_2 and 0.1120 gram H_2O.

II. 0.1509 gram substance gave 0.3445 gram CO_2 and 0.1114 gram H_2O.

III. 0.2009 gram substance gave the following data: $B = 759$, $t = 19°$, $v = 12.5$ cc.

	Calculated for $C_{11}H_{17}NO_5$.	Found, I.	II.	III.
C	62.56	62.45	62.26	...
H	8.06	8.29	8.19	...
N	6.63	...	...	6.89
O	22.75	...	...	...

V.—*Isobutylamine and Ethylic Acetosuccinate.*

10 grams of ethylic acetosuccinate were mixed with 3.4 grams of dry isobutylamine, and this yellow-colored mixture allowed to stand several days in the cold. At the end of two days a layer of water had collected on the upper surface of the liquid. The water was removed by means of a separating funnel and the residual liquid fractioned under diminished pressure. By far the greater part boiled constantly at 175° (temperature of paraffin-bath 195°) under a pressure of 15 mm., and on cooling solidified to a crystalline mass of needles. After recrystallisation from carbon bisulphide, snow-white needles melting at 68° were obtained. Analysis gave figures corresponding to the formula $C_{12}H_{19}NO_5$, that is, the lactam of α-isobutylamidoethylidenesuccinic ether.

I. 0.1528 gram substance gave 0.3597 gram CO_2 and 0.1192 gram H_2O.

II. 0.1612 gram substance gave 0.3771 gram CO_2 and 0.1243 gram H_2O.

III. 0.2020 gram substance gave the following data: $B = 760$, $t = 18°$, $v = 11.5$ cc.

	Calculated for $C_{12}H_{19}NO_5$.	Found, I.	II.	III.
C	64.00	64.20	63.79	...
H	8.44	8.67	8.57	...
N	6.22	...	...	6.57
O	21.33	...	...	...

VI.—*Amylamine and Ethylic Acetosuccinate.*

10 grams of ethylic acetosuccinate and 4 grams of amylamine were mixed with 5 cc. of absolute alcohol. This mixture, after standing two days at the ordinary temperature, was fractioned under diminished pressure. After alcohol and water had passed over, a fraction, boiling at 188° (temperature of paraffin-bath 205°) under a pressure of 16 mm., was obtained which, on cooling, gradually solidified to a snow-white mass of crystalline leaves. Upon recrystallisation from carbon bisulphide, colorless leaves, melting at 51°–52°, were obtained. These gave on analysis the following figures:

I. 0.1505 gram substance gave 0.3590 gram CO_2 and 0.1210 gram H_2O.

II. 0.1501 gram substance gave 0.3589 gram CO_2 and 0.1204 gram H_2O.

III. 0.2006 gram substance gave the following data: $B = 761$, $t = 19°$, $v = 10.7$ cc.

	Calculated for $C_{13}H_{21}NO_3$.	Found. I.	II.	III.
C	65.27	65.06	65.21	...
H	8.78	8.93	8.91	...
N	5.86	...	...	6.14
O	20.08	...	...	...

This substance is, as is shown by the above, the lactam of α-amylamidoethylidenesuccinic ether.

All the foregoing *substituted* lactams are extremely soluble in ether and carbon bisulphide, and, with the exception of the amyl derivative, crystallise in needles. If not perfectly pure they show a tendency to become yellow on keeping, and when treated with a dilute solution of barium hydrate they appear to suffer decomposition.

VII.—*Ammonia and Ethylic Acetomethylsuccinate.*

Ethylic acetomethylsuccinate was mixed with twice its volume of alcoholic ammonia saturated at 0°, and, after standing two days in a well-corked flask, the mixture was allowed to evaporate at the ordinary temperature. In the course of a few days the thick oily product began to crystallise very slowly until finally the whole became a mass of fine crystals. These were spread on

porous plates in order to free them from the mother-liquor. After two recrystallisations from warm acetic ether, in which the new substance is sparingly soluble, snow-white crystals, melting at 127°, were obtained. The analysis gave the following results:

I. 0.2010 gram substance gave the following data: $B=755$, $t=17°$, $v=13.7$ cc.

II. 0.2002 gram substance gave the following data: $B=755$, $t=21°$, $v=14$ cc.

III. 0.1511 gram substance gave 0.3288 gram CO_2 and 0.1010 gram H_2O.

	Calculated for $C_9H_{13}NO_3$.	I.	Found. II.	III.
C	59.02	...	...	59.34
H	7.10	...	...	7.42
N	7.65	7.85	7.89	...
O	26.23	...	...	...

The substance, therefore, has the formula $C_9H_{13}NO_3$, and is the lactam of α-amidoethylidenemethylsuccinic ether. Its formation may be represented by the equations

$$CH_3.CO.CH.CO_2R \quad CH_3.C(OH)CH.CO_2R$$
$$\quad\quad\quad | \quad\quad\quad\quad\quad | \quad\quad |$$
$$\quad\quad CH.CH_3 + NH_3 = \quad NH_2 \quad CH.CH_3$$
$$\quad\quad\quad | \quad\quad\quad\quad\quad\quad | \quad\quad |$$
$$\quad\quad CO_2R \quad\quad\quad\quad\quad\quad CO_2R$$

$$CH_3.C(OH)CH.CO_2R \quad CH_3.C=C.CO_2R$$
$$\quad\quad | \quad\quad | \quad\quad\quad\quad | \quad\quad |$$
$$\quad NH_2 \quad CH.CH_3 = \quad NH_2 \quad CH.CH_3 + H_2O.$$
$$\quad\quad\quad | \quad\quad\quad\quad\quad | \quad\quad |$$
$$\quad\quad CO_2R \quad\quad\quad\quad\quad CO_2R$$

$$CH_3.C=C.CO_2R \quad CH_3.C=C.CO_2R$$
$$\quad\quad | \quad\quad | \quad\quad\quad\quad | \quad\quad |$$
$$\quad NH_2 \quad CH.CH_3 = \quad\quad NH \quad CH.CH_3 + R.OH.$$
$$\quad\quad\quad | \quad\quad\quad\quad\quad\quad \diagdown / \quad\quad |$$
$$\quad\quad CO_2R \quad\quad\quad\quad\quad\quad\quad CO$$

The new compound is isomeric with that lactam which is formed by the action of methylamine on ethylic acetosuccinate. It appears quite remarkable that the formation of the amido-ether as intermediate product in this reaction remained unnoticed. The great tendency to lactam-formation, by which alcohol is split off, evidently depends upon the presence of the methyl-rest.

VIII.—*Ammonia and Ethylic Acetophenylsuccinate.*

Ethylic acetophenylsuccinate is described by Weltner[1] as crystallising in plates which melt at 75°–76°. I have prepared this ether by the action of phenylbromacetic ether on ethylic sodium-acetoacetate, and have invariably observed it in the form of needles, melting, as above, at 75°–76°.

By the action of alcoholic ammonia on ethylic acetophenylsuccinate, I found it convenient to use two volumes of the former and one of the latter. Both are kept in a well-corked flask, which from time to time is shaken vigorously in order to bring about a solution of the ether in the alcoholic ammonia. This is generally effected in about two days, after which the solution is allowed to evaporate in open dishes. Diamond-shaped plates soon begin to separate from the liquid until finally the whole becomes a mass of crystals. These may be freed from the mother-liquor by drying on porous plates. After several recrystallisations from hot acetic ether, in which the substance is soluble with difficulty, snow-white crystals, melting at 147°–149°, were obtained. It was, however, observed that if the substance be very slowly heated to 127°–128° and there held for a few moments, the substance melted at that temperature. The analysis gave the following results:

I. 0.1530 gram substance gave 0.3603 gram CO_2 and 0.0915 gram H_2O.

II. 0.1205 gram substance gave 0.2840 gram CO_2 and 0.0737 gram H_2O.

III. 0.1500 gram substance gave 0.3538 gram CO_2 and 0.0906 gram H_2O.

IV. 0.1509 gram substance gave 0.3565 gram CO_2 and 0.0902 gram H_2O.

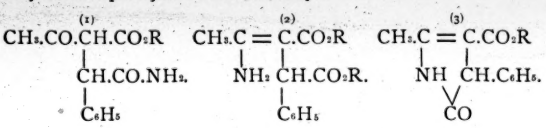
V. 0.1509 gram substance gave 0.3562 gram CO_2 and 0.0902 gram H_2O.

VI. 0.2022 gram substance gave the following data: $B = 758.5$, $t = 19°$, $v = 9.8$ cc.

	Calculated for			Found.					
	(1) $C_{14}H_{17}NO_4$.	(2) $C_{18}H_{21}NO_4$.	(3) $C_{14}H_{18}NO_3$.	I.	II.	III.	IV.	V.	VI.
C	63.87	65.98	68.57	64.22	64.28	64.33	64.43	64.37	...
H	6.46	7.21	6.12	6.64	6.79	6.71	6.64	6.64	...
N	5.32	4.81	5.71	...	...	...	...	...	5.56
O	24.33	21.99	19.59	...	...	...	...	...	...

[1] Ber. d. chem. Ges. **17**, 71.

The empirical formulæ represent three of the possible compounds which might be formed by the action of ammonia on ethylic acetophenylsuccinate, namely :



The results of analysis do not, however, show the necessary degree of conformity with any of these formulæ ; it is therefore probable that the substance is either difficult to obtain in a state of purity or not easy of combustion. The readiness with which it gives the lactam [formula (3)] on heating confirms the belief that it must be constituted either according to formula (1) or according to formula (2). Which of the two is the correct one I have as yet been unable to decide.

In order to prepare the lactam, the product obtained by the action of ammonia on the ethylic acetophenylsuccinate is heated for a short time at 160° in a paraffin-bath, or until the evolution of alcohol vapors has ceased. It is then dissolved in hot acetic ether, in which it is sparingly soluble, and from this medium crystallises in snow-white needles. Two recrystallisations are generally necessary, before the substance can be obtained in a state of purity. It melts at 127°–128°, is quite readily soluble in alcohol and in ether, more sparingly in ethylic acetate and carbon bisulphide. Analysis led to the formula $C_{14}H_{15}NO_3$.[1]

I. 0.1238 gram substance gave 0.3130 gram CO_2 and 0.0718 gram H_2O.

II. 0.1240 gram substance gave 0.3120 gram CO_2 and 0.0707 gram H_2O.

III. 0.1242 gram substance gave 0.3142 gram CO_2 and 0.0726 gram H_2O.

IV. 0.1710 gram substance gave the following data : $B=745$, $t=17°$, $v=8.6$ cc.

V. 0.2014 gram substance gave the following data : $B=755$, $t=19°$, $v=10.4$ cc.

[1] It appears to me quite probable that Weltner (Ber. d. chem. Ges. **18**, 795) has already prepared this compound, although only in small quantity. He describes the substance as crystallising in needles and melting at 128°–129°, but was unable, however, from the results of his analysis to determine its constitution.

	Calculated for $C_{14}H_{13}NO_3$.	Found. I.	II.	III.	IV.	V.
C	68.57	68.95	68.63	68.99	...	...
H	6.12	6.44	6.33	6.49	...	...
N	5.71	...	...	...	5.73	5.89
O	19.59	...	...	...	...	...

From the results of the analysis it is, then, evident that this compound is to be regarded as the lactam of *α*-amidoethylidenesuccinic ether, and is formed by the action of ammonia on ethylic acetophenylsuccinate according to the equation

$$\begin{array}{l} CH_3.CO.CH.CO_2R \\ \qquad\quad | \\ \qquad CH.C_6H_5 \\ \qquad\quad | \\ \qquad CO_2R \end{array} + NH_3 = \begin{array}{l} CH_3.C=C.CO_2R \\ \qquad\quad | \quad\ | \\ \qquad NH \quad CH.C_6H_5 \\ \qquad\quad \diagdown / \\ \qquad\quad CO \end{array} + H_2O + R.OH.$$

On heating with a dilute solution of barium hydrate, a very beautiful salt is obtained, which is probably the barium salt of *α*-amidoethylidenesuccinic acid.

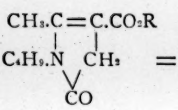
For the sake of comparison, it was thought advisable to summarise the lactams described in the foregoing pages, as well as all others of a similar constitution which are thus far known.

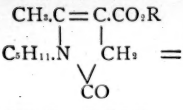
$$\begin{array}{l} CH_3.C=C.CO_2R \\ \qquad | \quad\ | \\ \qquad NH \ CH_2 \\ \qquad \diagdown / \\ \qquad CO \end{array} = \text{lactam of } \alpha\text{-amidoethylidenesuccinic ether.}$$

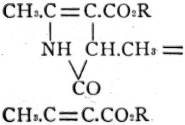
$$\begin{array}{l} CH_3.C=C.CO_2R \\ \qquad | \quad\ | \\ CH_3.N \ CH_2 \\ \qquad \diagdown / \\ \qquad CO \end{array} = \text{lactam of } \alpha\text{-methylamidoethylidenesuccinic ether.}$$

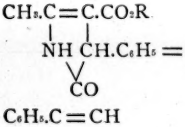
$$\begin{array}{l} CH_3.C=C.CO_2R \\ \qquad | \quad\ | \\ C_2H_5.N \ CH_2 \\ \qquad \diagdown / \\ \qquad CO \end{array} = \text{lactam of } \alpha\text{-ethylamidoethylidenesuccinic ether.}$$

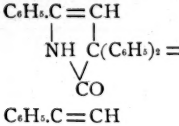
$$\begin{array}{l} CH_3.C=C.CO_2R \\ \qquad | \quad\ | \\ C_3N_7.N \ CH_2 \\ \qquad \diagdown / \\ \qquad CO \end{array} = \text{lactam of } \alpha\text{-propylamidoethylidenesuccinic ether.}$$

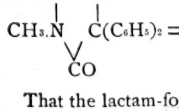

= lactam of α-isobutylamidoethylidenesuccinic ether.


= lactam of α-amylamidoethylidenesuccinic ether.

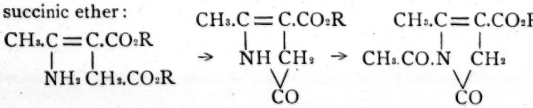

= lactam of α-amidoethylidenemethylsuccinic ether.


= lactam of α-amidoethylidenephenylsuccinic ether.


= lactam of α-diphenyl-γ-phenyl-γ-amidoisocrotonic acid. 3-diphenyl-5-phenylpyrrolone.[1]

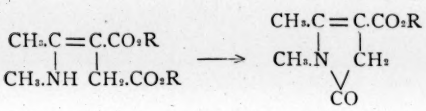

= lactam of α-diphenyl-γ-phenyl-γ-methylamidoisocrotonic acid. 1-methyl-3-diphenyl-5-phenylpyrrolone.[1]

That the lactam-formula which has been exclusively employed in the foregoing is the correct one for the condensation-products arising from the action of ammonia and alkylamines on ethylic acetosuccinate is proven, first, by the formation of an acetyl derivative from the condensation-product of α-amidoethylidenesuccinic ether:

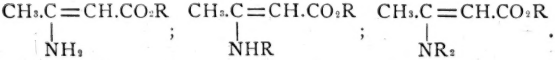

;

and, secondly, by the formation of the lactam of α-methylamidoethylidenesuccinic ether:

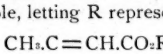
[1] Japp, Klingemann: Ber. d. chem. Ges. **22**, 2884.

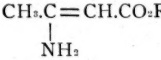


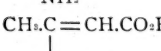
So far as the nomenclature of such ammonia- and alkylamine-derivatives of β- and γ-ketonic ethers is concerned, I believe one should be governed somewhat by the following: There can no longer be any doubt that the products formed by the action of ammonia and alkylamines on ethylic acetoacetate are constituted according to the general formulæ:

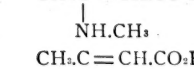


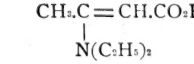
It would therefore be consistent to name them accordingly, for example, letting R represent the ethyl group —

 , ethylic β-amidocrotonate;[1]

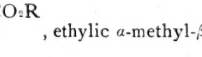
 , ethylic β-methylamidocrotonate;[2]

 , ethylic β-diethylamidocrotonate;[3]

 , ethylic α-methyl-β-amidocrotonate;[3]

 , ethylic α-ethyl-β-amidocrotonate.[3]

The products formed by the action of ammonia and alkylamines on ethylic acetosuccinate may be conveniently derived from the as-yet-unknown ethylidenesuccinic ether,



[1] Collie: Ann. Chem. (Liebig) **226**, 321. [2] Kuckert: Ber. d. chem. Ges. **18**, 618.

[3] The names given to these substances by Conrad and Epstein (Ber. d. chem. Ges. **20**, 3055) —amidomethylacetoacetic ether, amidoethylacetoacetic ether, and amidoacetosuccinic ether— appear to me to be inappropriate, inasmuch as these substances do not have the character of acetyl compounds; they do not even possess an acetyl-rest.

The ammonia derivative would accordingly be represented by the formula

$$\begin{array}{l} CH_3.C = C.CO_2R \\ \quad\;\; | \quad\;\; | \\ \quad NH_2 \; CH_2.CO_2R \end{array} = \text{ethylic } \alpha\text{-amidoethylidenesuccinate};^{1}$$

that of methylamine,

$$\begin{array}{l} CH_3.C = C.CO_2R \\ \quad\;\; | \quad\;\; | \\ CH_3.NH \; CH_2.CO_2R \end{array} = \text{ethylic } \alpha\text{-methylamidoethylidenesuccinate.}$$

The condensation-product would simply be the lactam of that amido compound from which it was formed; for example:

$$\begin{array}{l} CH_3.C = C.CO_2R \\ \quad\;\; | \quad\;\; | \\ \quad NH \quad CH_2 \\ \quad\;\; \diagdown\!\diagup \\ \quad\;\; CO \end{array} = \text{lactam of } \alpha\text{-amidoethylidenesuccinic ether;}$$

$$\begin{array}{l} CH_3.C = C.CO_2R \\ \quad\;\; | \quad\;\; | \\ CH_3.N \quad CH_2 \\ \quad\;\; \diagdown\!\diagup \\ \quad\;\; CO \end{array} = \text{lactam of } \alpha\text{-methylamidoethylidenesuccinic ether;}$$

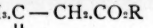
$$\begin{array}{l} CH_3.C = C.CO_2R \\ \quad\;\; | \quad\;\; | \\ \quad NH \; CH.CH_3 \\ \quad\;\; \diagdown\!\diagup \\ \quad\;\; CO \end{array} = \text{lactam of } \alpha\text{-amidoethylidenemethylsuccinic ether.}$$

Of course these lactams could as fittingly be named from the hypothetical base pyrrolone, $\begin{array}{l} CH = CH \\ \quad | \quad\;\; | \\ NH \quad CH_2 \\ \quad\;\; \diagdown\!\diagup \\ \quad\;\; CO \end{array}$, as those products which Japp and Klingemann[2] obtained by the action of ammonia and methylamine on α-β-dibenzoylstyrol. However, the name lactam reminds one more of the method of formation and of the general character of the substances described above, and is therefore to be preferred to the expression pyrrolone. I should here like to call attention to the fact that, if there are sufficient reasons for assuming that the products formed by the action of ammonia, methyl- and diethyl-amine on ethylic acetoacetate,—

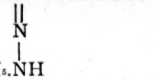
$$\begin{array}{l} CH_3.C = CH.CO_2R, \\ \quad\;\; | \\ \quad NH_2 \end{array} \quad \begin{array}{l} CH_3.C = CH.CO_2R, \\ \quad\;\; | \\ \quad NH.CH_3 \end{array} \quad \begin{array}{l} CH_3.C = CH.CO_2R, \\ \quad\;\; | \\ \quad N(C_2H_5)_2 \end{array},—$$

[1] Conrad, Epstein: Ber. d. chem. Ges. **20**, 3055. [2] Ber. d. chem. Ges. **22**, 2884.

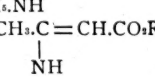
are derivatives of ethylic β-amidocrotonate; the same reasons justify the assumption that the substance formed by the action of phenylhydrazine on ethylic acetoacetate is not, as Knorr[1]



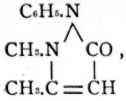
assumes, β-phenylhydrazidobutyric ether,



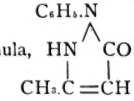
but rather β-phenylhydrazidocrotonic ether,



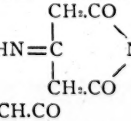
For Knorr has, by the action of symmetrical methylphenylhydrazine on ethylic acetoacetate, succeeded in preparing the same phenyldimethylpyrazolone, the so-called antipyrine,[2]



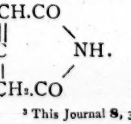
which is formed by the action of methyl iodide on phenylmethylpyrazolone. It is difficult to understand why symmetrical methylphenylhydrazine should act on ethylic acetoacetate in a different manner from phenylhydrazine itself. It is therefore probable that the product arising from the condensation of β-phenylhydrazidocrotonic ether has the constitutional formula,



For similar reasons it is highly probable that the condensation-product obtained by the action of ammonia on acetonedicarbonic ether, the so-called glutazine, which Stokes and Pechmann[3] believe to be the imide of β-imidoglutaric acid,



is the imide of β-amidoglutaconic acid,



[1] Ann. Chem. (Liebig) **238**, 151, 160. [2] Ibid. **238**, 151, 160. [3] This Journal **8**, 389.

By the action of a dialkylamine on acetonedicarbonic ether it would perhaps be possible to render an easy solution of this problem.

As a further generalisation of the reactions described above appears desirable, I have already begun a study of the action of ammonia and alkylamines on some other γ-ketonic ethers. I also intend to investigate the action of ammonia on a few δ-ketonic ethers, for example, α-acetoglutaric ether,

$$\begin{array}{l} CH_3.CO.CH.CO_2R \\ \quad\quad\quad\quad\quad | \\ \quad\quad\quad\quad\quad CH_2 \\ \quad\quad\quad\quad\quad | \\ \quad\quad\quad\quad\quad CH_2.CO_2R \end{array},$$

as well as α-acetotricarballylic ether,

$$\begin{array}{l} CH_3.CO.CH.CO_2R \\ \quad\quad\quad\quad\quad | \\ \quad\quad\quad\quad\quad CH.CO_2R \\ \quad\quad\quad\quad\quad | \\ \quad\quad\quad\quad\quad CH_2.CO_2R \end{array}.$$

CHEMICAL LABORATORY, BONN UNIVERSITY.

THE SEPARATION OF TITANIUM, CHROMIUM, ALUMINUM, IRON, BARIUM AND PHOSPHORIC ACID IN ROCK ANALYSIS.

BY THOMAS M. CHATARD.

Having to examine some magnesian silicate rocks containing, in addition to iron and aluminum, small quantities of titanium, chromium, barium and phosphoric acid, the methods for the decomposition of such rocks and the separation of their constituents were studied and compared so as to determine the most advisable manner of procedure. After repeated trials the following course, combining a number of well-known methods, has been found to be the most satisfactory.

The silica and bases are determined by the ordinary sodium carbonate fusion method, in which the hydrates of titanium, chromium, iron and aluminum, together with the phosphoric acid, are

precipitated together, and, after weighing, fused with sodium bisulphate, dissolved, the small amount of silica separated, and the solution, after reduction of the ferric oxide, titrated for total iron.

To separate these oxides and at the same time to determine the barium, two grams of the finely pulverised mineral are put into a platinum crucible or dish, moistened with water, dilute sulphuric acid (1 : 1) and pure strong hydrofluoric acid added in considerable excess, the vessel put on a radiator to evaporate, and stirred from time to time. When the solution is so far evaporated that fumes of sulphuric acid begin to come off, there should still be so much acid present as to form a solution or emulsion and not a paste, since the paste is liable to bake on the bottom of the vessel and form the difficultly-soluble anhydrous sulphates produced by overheating, especially when magnesia is present in quantity. At this point it is well to add a few drops of nitric acid to oxidise the ferrous oxide, and a little more hydrofluoric acid to insure the complete expulsion of the silica. The evaporation is then continued until the sulphuric acid fumes strongly and no odor of hydrofluoric acid can be detected when the solution is cooled below the point at which the sulphuric acid fumes.

About 25 cc. of dilute hydrochloric acid (1 : 5) is now added, the stirring being continued, and the material is then evaporated on the water-bath until most of the hydrochloric acid has been driven off. The material is then washed into a beaker, and any residue adhering to the vessel can be removed by a few drops of hot, strong hydrochloric acid, the vessel being rubbed with a bit of paper if necessary. If the solution be very turbid it can be digested on the water-bath for some time, but ultimately it is diluted with hot water to 250–300 cc., allowed to stand for several hours, and then filtered.

The residue contains the barium as sulphate, and sometimes small amounts of chromite or other minerals of the same class. It is washed, ignited and thoroughly fused with sodium carbonate in a small crucible, the fused mass being then digested with hot water and leached. The well-washed residue is dissolved on the filter with dilute hydrochloric acid, and this solution filtered through the same filter, which, after washing, is burned, the ash fused with a little sodium carbonate, the mass dissolved in dilute hydrochloric acid and added to the leachings, which are now acidified and added to the main solution, after reduction of the

chromic acid. The hydrochloric acid solution containing the barium is evaporated to a few drops to get rid of the excess of acid, diluted, the barium precipitated, and the filtrate from the barium sulphate added to the main solution.

This main solution, which should be perfectly clear and contain the iron and chromium as sesquioxides, is now made alkaline by ammonia and the precipitate redissolved by dilute hydrochloric acid. A few drops of acetic acid are added, the liquid brought to a boil, ammonia added in very slight excess, the boiling continued for a few minutes and the precipitate filtered and washed. As the sole reason for this precipitation is to get rid of the magnesia and the accumulation of other salts, the washing need not be thorough, but the filtrate must be tested and the precipitation proved complete.

The precipitate is dissolved in hot dilute hydrochloric acid. The filter after washing is burned in a large platinum crucible, into which the solution, concentrated to a small bulk, is put and evaporated on the water-bath till it becomes pasty. Just enough water is now added to dissolve the salts, and then dry sodium carbonate is added in small portions, with continual stirring, till a comparatively dry mass results. This must be carefully done, for if too much soda is added at a time, and each addition is not thoroughly stirred into the mass, the after fusion is apt to be "lumpy" and unsatisfactory.

When a good excess of carbonate has thus been added, the mass is dried and gradually brought to clear fusion, which should be continued for half an hour. If lumps form, which is, however, rarely the case if lime and magnesia are absent and the foregoing directions are followed, they can be broken up by shaking the crucible with a circular motion to detach them from its walls. When the fusion is complete, the mass is spread around the walls of the crucible and slightly cooled. A small quantity of sodium nitrate is now added, the whole rapidly fused and carefully boiled for not more than five minutes; it is then again spread over the crucible and rapidly cooled with a blast of air. The mass is boiled with water till completely disintegrated, and then leached; repeated tests have shown that the residue which contains the titanium is, when well washed, free from chromium and phosphoric acid.

The washed residue is dissolved in hot dilute hydrochloric acid, the filter burned, the ash fused with sodium bisulphate, dissolved in water and added to the solution. The titanium in this solution

is separated by the excellent method of Dr. Gooch,[1] all the details as laid down by him being followed. I have, however, found it convenient, after the destruction of the tartaric acid by potassium permanganate, and the clearing of the solution by sulphurous acid, to add ammonia in slight excess, then at once acetic acid in excess, and boil with addition of sulphurous acid. The precipitate of titanium hydrate, mixed with some alumina, is filtered and washed with water containing sulphurous acid and a little acetic acid. It is thus freed from manganese and brought into a small compass, rendering the after work easier. Before the final precipitation of the titanium the platinum generally in the solution should be removed by hydrogen sulphide.

The filtrate containing the chromic and phosphoric acids is heated, and ammonium nitrate cautiously added till no further precipitation of alumina occurs. The precipitation of the aluminum phosphate seems to be complete, but some alumina always remains in solution. The precipitate is allowed to settle, the supernatant liquid decanted and the precipitate washed with a solution of ammonium nitrate until the yellow tinge disappears; it is then dissolved in dilute nitric acid, and the phosphoric acid precipitated by molybdate solution.

The filtrate containing the chromic acid is acidified, boiled, neutralised with ammonia, and the chromium precipitated by freshly prepared ammonic sulphide. The precipitate, after some washing, is dissolved in hot dilute nitric acid, and, after concentration, potassium chlorate is added, the solution boiled, and finally evaporated nearly to dryness to expel the excess of acid. It is then diluted with cold water, and a saturated solution of sodium bicarbonate added in small excess, separating the last traces of alumina. After standing about three hours, the alumina is filtered and washed with moderately dilute solution of the bicarbonate. The filtrate is acidified and the chromic acid reduced and precipitated by ammonium sulphide in a platinum dish, filtered, washed, redissolved to get rid of traces of alkali, reprecipitated, and finally weighed as chromic oxide.

This method, due to Baubigny, for the separation of aluminum from chromium is very good and convenient if the solution be free from iron and contain but little alumina. Careful tests have shown that if iron be present some of it always remains in solu-

[1] Proc. Am. Acad. 12, 435 seq. (Bull. No. 27, U. S. G. S., p. 16 seq.).

tion, while if there be much alumina it is almost impossible to wash out all of the chromate from the bulky precipitate with the cold solution of bicarbonate which must be used. It must also be noted in this connection that a solution of iron and chromium prepared by the Baubigny method was made ammoniacal, and it was proved that while all of the iron was precipitated, this precipitate, even after the most careful washing with hot water, contained chromium.

Although the number of details in this process may seem very great, experience has shown that none of them can safely be neglected for the purpose of shortening the work; if the whole process be carefully followed out, the results are very satisfactory, as shown by the following tests on a typical magnesian rock:

	Percentage Cr_2O_3.	TiO_2.	BaO.	P_2O_5.
No. 1,	.270	.46	.040	.375
No. 2,	.285	.39	.060	.385
No. 3,	.317	.46	.055	...
No. 4,	.280	...	...	...
Average,	.288	.44	.052	.380

The use of sodium nitrate for the fusions is not absolutely necessary, though one is more sure of complete oxidation if it be employed. In the analysis of chrome ores the best results have been obtained by fusing the finely-pulverised ore with sodium carbonate alone, but keeping it in clear fusion for an hour. The fused mass is treated like an ordinary silicate fusion, the silica after weighing being volatilised by hydrofluoric acid, and the residue, usually small, again fused with sodium carbonate, giving a clear solution in hydrochloric acid.

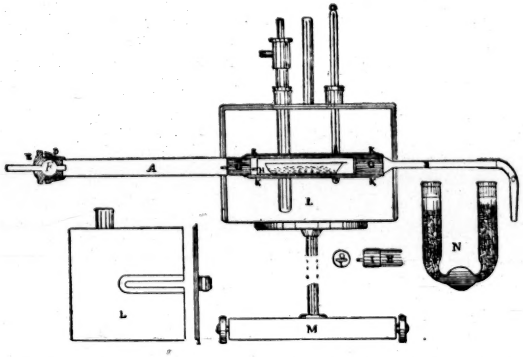
AN APPARATUS FOR THE DETERMINATION OF WATER IN MINERAL ANALYSIS.

By Thomas M. Chatard.

In all cases where the water in minerals and rocks is easily expelled, the apparatus described by me in another place[1] has

[1] Am. J. Sci. **37**, 468 (Bulletin No. 60, U. S. G. S., p. 86).

been found very satisfactory. Many rocks and minerals, however, do not lose all of the water until heated for a considerable time at a temperature at which glass softens. A more refractory tube is therefore necessary, and a platinum tube, such as is used for the determination of carbon in iron and steel, has been employed to great advantage. The arrangement of the apparatus is shown in the cut.



The tube *A* has an outside diameter of 16 mm.; the small tube *B*, 5 mm. *A* need not be longer than 250–300 mm.; *B*, 80 mm. *C* is a piece of lead glass tube fused on to the end of *B* and bent and drawn out as shown. *D* is a collar of phosphor-bronze bored out with a slight taper and fitted over the end of the platinum tube, the edge of which is flanged smoothly over the face of the collar. The phosphor-bronze plug *E* has a taper corresponding to that of the collar, which it fits tightly and smoothly. The shoulders of both plug and collar are made hexagonal to insure a firm grasp when putting together or taking apart, and should be stout enough to prevent any accidental deformation. The small tube *F* is closed at the inner end, a ring of small holes being bored through the side close to the face of the plug. By this arrangement all back circulation is prevented, and the moisture which condenses in the cold part of the tube is easily and completely removed.

The platinum boat containing the substance to be examined is

placed in the cylinder *H*, made of platinum foil, which is closed at one end by a cap *I*, in the center of which is a small hole to allow the passage of the air current over the substance, while a small ring soldered to the cap permits an easy withdrawal of the cylinder. The use of this cylinder prevents a loss of any of the substance by spattering, as when sodium carbonate is mixed with it, and also the frequently resulting adhesion of the boat to the tube.

The permeability of highly-heated platinum to the gases of combustion, resulting in errors in the determination, is well known. To overcome this and also to protect the valuable tube from injury, the part where the cylinder is placed, and which is ultimately exposed to the highest heat of a blast lamp, is wrapped with several layers of asbestos paper soaked with a saturated solution of borax. The wrapping is secured with thread and dried, more borax solution being put on if deemed necessary. When quite dry, the asbestos is covered with a sheet of platinum foil *KK* secured with wire, highly heated and cooled slowly; if properly made and put on, such a wrapping should last for months of steady use, can be easily replaced when necessary, and all risk of injury to the tube is avoided.

The air-bath *L* specially constructed for this tube is a copper box, open in front with a slit at either end, as shown in *L'*, suited to the size of the two portions of the tube. The front is closed by a plate of copper, on the inner side of which several layers of asbestos board are fastened. The edges of these are slightly beveled to insure a tight fit, and a hook at the top of the bath holds the plate in place. The bath is covered with asbestos board, and, when in use, the open portions of the slits are closed by asbestos plugs. It is furnished with thermostat, thermometer and lamp, and is mounted on a stand, the base of which (*M*) is fitted with four small wheels, so that the arrangement can be pushed into position or removed without disturbing the rest of the apparatus.

When making a determination, the tube is fastened by a clamp near the end, the roll of platinum gauze *G* shoved into place, the plug inserted, and a slow stream of dry air passed through the tube, which is then heated by passing a lamp along the entire length, and allowed to cool. The boat containing the substance is now put into the cylinder, which is at once pushed into the tube till it touches the roll of gauze; the roll *G'* follows and the plug reinserted, the current of air being kept up. The air-bath, pre-

viously brought up to its standard temperature, 105°, is now opened, run into position, the tube sliding smoothly into the slits, and then closed, regaining its temperature in a few minutes. When it is considered that the tube and contents are thoroughly dry, the U-tube *N*, described in the paper already quoted, is attached, and the air-bath removed by opening it and rolling it back. The tightness of the apparatus is now tested, and, if satisfactory, the air current is regulated and the tube gradually heated, beginning at the roll *G'*, and using an ordinary burner. If much water condenses in the bent glass tube the heat must be very gradually increased, and this is best effected by keeping the part *G'* quite hot, thus heating the air current and preventing, as far as possible, the always-annoying back-circulation. Finally, the portion of the tube covered by the borax-asbestos is exposed to the full heat of a blast lamp to which a flat burner has been adapted.

When no moisture remains in the glass tube, the blast lamp is removed and the apparatus allowed to cool. When cold the U-tube is disconnected and weighed, and the cylinder with its contents withdrawn. If the amount of material at disposal is small, this portion can be used for the determination of the silica and the bases, since any loss has been prevented by the cylinder, which can be washed clean with dilute hydrochloric acid, and any insoluble matter filtered off and added to the rest of the substance in the boat, which can be fused with sodium carbonate in the usual manner.

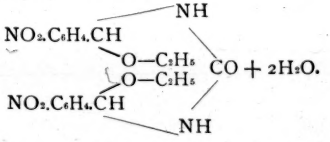
The use of the cylinder and the asbestos wrapping obviates the only serious objection to the use of this method, namely, the high cost of the platinum tube, as in this way the tube is absolutely protected from all damage. By having duplicate boats, cylinders, and U-tubes, the determinations can be made quite rapidly, and a large number of determinations made in this way by myself and others have given very satisfactory results.

ON BENZYLIDENEBIURET AND CHLORBENZYLIDENETHIOBIURET.

By John J. Abel.

About a year and a half ago, Dr. Ernst Lüdy[1] described a method for detecting small quantities of urea, depending upon the fact that if orthonitrobenzaldehyde be added to an alcoholic solution of urea and the mixture then evaporated to dryness on the water-bath, the aldehyde combines with the urea to form nitrobenzylidenediureïd, in accordance with the following equation:

$$2C_6H_4(NO_2)CHO + CO(NH_2)_2 + 2C_2H_5OH =$$



An excess of either urea or orthonitrobenzaldehyde does not in any way affect the reaction, as the diureïd is always formed when alcoholic solutions of these two bodies are mixed and evaporated to dryness. The resulting orthonitrobenzylidenediureïd is very slightly soluble in cold or in hot water, in alcohol or in ether, and this fact condemns it as a reagent for quantitative purposes. On the other hand, the delicacy of this reaction is such that good use can be made of it in qualitative work. Thus Lüdy was able to detect urea in solutions containing less than two milligrams. For instance 0.02 cc. of an alcoholic extract containing in this volume only 0.00109 gram urea gave the diureïd reaction. When the orthonitrobenzylidenediureïd has formed in an alcoholic extract containing urea, the next step is to wash away an excess of either orthonitrobenzaldehyde or of urea, and then to split up the diureïd with a 10 per cent. solution of sulphuric acid. The presence of the orthonitrobenzaldehyde thus set free is demonstrated by adding a little phenylhydrazine hydrochlorate, when the resulting phenylosazone at once causes the acidulated fluid to take on a beautiful deep-red color. I may remark in passing that Pickel[2] first showed that the three isomeric mono-

[1] Sitzungsber. d. kais. Akad. d. Wiss. in Wien, Bd. **98**, Abth. II, b, p. 206.
[2] Ann. Chem. (Liebig) **232**, 232.

nitrobenzaldehydes all form phenylosazones with phenylhydrazine, and Lüdy seems to have overlooked this earlier investigation.

A compound of urea easily formed and entirely insoluble in water, is still a desideratum of analytic chemistry, and the great usefulness of such a body, could it be found, in medical science especially, justifies a search for it. Therefore I gladly accepted the invitation of Prof. v. Nencki of the University of Berne to investigate the action of benzaldehyde on urea with a view to securing a product entirely insoluble in either alcohol or water. However, experiments soon showed that no insoluble condensation-product is formed in alcoholic or aqueous solutions of urea to which benzal chloride has been added. A reaction takes place only when the alcohol and water have been driven off and the point of dry heat is reached. On careful examination it was found that the resulting body is benzylidenebiuret. Now, although this body is of no use for the quantitative estimation of urea, or even for qualitative purposes, yet it was of interest more carefully to study its properties and the best way for preparing it. I obtained the best output by heating an excess of urea, say three equivalents with one equivalent of benzal chloride in a flask on the sand-bath until the thermometer registered 198° or 200° C. The beginning of the reaction is easily recognised by the appearance of gas bubbles at the boundary line between the molten urea and the benzal chloride. When the temperature has reached 198°–200° the reaction is at its height; the source of heat must now be removed and the reaction left to itself until it is complete. The contents of the flask are soon converted into a solid mass, and when this has cooled to about 100°, boiling water is poured into the flask, and the granular mass is well stirred and the solution filtered. The white mass remaining in the flask and on the filter is treated several times with hot alcohol and decanted. The substance now remaining is largely freed from the by-products of the reaction and must be dissolved in hot water, very large quantities of which are necessary. Out of this aqueous solution large, glistening rhombic prisms crystallise when the conditions are favorable to a slow crystallisation; otherwise clusters of fine needles are formed. The aqueous and alcoholic solutions filtered from the crude product also yield these crystals, mingled, however, with much ammonium chloride.

The empirical formula of benzylidenebiuret as determined by

analysis of the large rhombic crystals, several times recrystallised, and by molecular-weight determinations according to Raoult's method, is $C_9H_9N_3O_2$. Inasmuch as ammonium chloride and cyanic acid are the only by-products of the reaction, it may be expressed in the terms of the following equation:

$$C_6H_5.CHCl_2 + 3CO.N_2H_4 = C_9H_9N_3O_2 + 2NH_4Cl + CNOH.$$

Combustion analyses of the large crystals, twice crystallised and dried at 110° C. until of constant weight, gave the following results:

I. 0.2898 gram substance gave 0.6 gram CO_2 and 0.1372 gram H_2O.

II. 0.2463 gram substance gave 0.5085 gram CO_2 and 0.1087 gram H_2O.

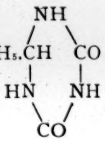
III. 0.248 gram substance gave 51 cc. N at 16° C. and 711 mm. pressure = 0.0555 gram N; or, by percentage,—

	I.	II.	III.	Required for $C_9H_9N_3O_2$.
C	56.77	56.30	...	56.54
H	5.26	4.90	...	4.71
N	...	...	22.39	21.98

As the body is sufficiently soluble in phenol, molecular-weight determinations according to Raoult's method were made in the manner already described by me.[1] 0.3204 gram substance was dissolved in 12.737 grams phenol, and the freezing point was found to be lowered by 0.96°. The molecular weight of the body therefore, determined according to Raoult's formula, $M = \frac{T.P.100}{D.L.}$, is 199. In a second experiment, 0.4434 gram substance was dissolved in 21.022 grams phenol, and the resulting depression of the freezing point amounted to 0.78°, and M was found to be 205. The empirical formula $C_9H_9N_3O_2$ demands for M 191. The melting point of the body lies at 258° C., uncorrected, and at this temperature decomposition occurs.

Whether the benzylidene substitutes two hydrogen atoms in the same amidogen group and the resulting biuret is to be represented by the formula $C_6H_5-CH=N-CO-NH-CO-NH_2$, or whether the substitution occurs in the manner indicated by the

[1] Sitzungsber. d. kais. Akad. d. Wiss. in Wien. **99**, Abth. II, 79-80.

following closed formula,  is not easily decided.

Of the two structural formulæ, the latter is probably the correct one, for the body is not more soluble in dilute mineral acids than in water, and this speaks against the presence of an amidogen group. On the other hand, I was not able to get a nitrosamine by treating the body with potassium nitrite or amyl nitrite.

Aqueous solutions of benzylidenebiuret are precipitated by most metallic salts. Thus, mercuric chloride gives a precipitate consisting of white granules, which, examined under the microscope, are seen to be aggregates of small, pointed crystals. The chloroplatinate obtained by precipitating an aqueous solution with a 5-per cent. solution of platinum chloride, crystallises in thin plates of rhombic form. Chloride of iron yields a double salt, which crystallises in thin, glistening plates.

With regard to the solubility of the body, I may say that it is partially soluble in phenol, in hot water, and in alcohol; very slightly, or not at all, in ether and chloroform, and insoluble in carbon bisulphide.

In order to study the action of hydrolytic agents upon benzylidenebiuret, I treated it with dilute sodium hydroxide, and also with barium hydroxide. When boiled with a dilute solution of the former, ammonia is evolved and the odor of benzaldehyde is noticed. In order to study the decomposition products resulting from treatment with caustic alkalis, I proceeded as follows:

60 grams of barium hydroxide were dissolved in 400 grams of hot water, filtered, and poured upon 4 grams of the substance previously put into a liter flask to which a reflux condenser was attached, and the whole kept at a boiling heat on the sand-bath for four hours, after which the white sediment which had formed was filtered off while hot.

During the boiling the odor of benzaldehyde is very marked, and a piece of moistened litmus paper held in the current of escaping steam is turned blue. The filtrate was kept warm on the water-bath and carbon dioxide passed through it until a test-filtrate showed that it was fairly free from barium precipitable by

a current of carbon dioxide. It was then set aside for ten hours and again heated on the water-bath, while carbon dioxide was again passed through until all the barium removable in this way was precipitated. The clear filtrate was now evaporated to dryness on the water-bath, the residue dissolved in a very little water and treated with hydrochloric acid. The crystalline precipitate thus produced was several times recrystallised out of hot water, and when sufficiently purified was, through a study of its melting point, crystalline form and capability of sublimation, proved to consist of benzoic acid. The fluid remaining after precipitating the benzoic acid with hydrochloric acid, was evaporated on the water-bath and treated with alcohol. By Lüdy's method the presence of urea in the alcoholic extract was easily shown. But the urea was also isolated and its identity established by its crystalline form, by the characteristic crystals of its nitrate, and by the fact of its giving the biuret reaction and yielding ammonia when treated with hot sodium hydroxide. Therefore boiling this body with barium hydroxide causes it to split up, while taking up water, according to the following equation:

$$C_9H_9N_3O_2 + 3H_2O = C_6H_5.CHO + CO\langle\begin{matrix}NH_2\\NH_2\end{matrix} + NH_4OH + CO_2.$$

I will add that, if it be dissolved in concentrated sulphuric acid and then diluted with water, a compound crystallises out in large clusters of rhombic prisms.

Inasmuch as urea and benzal chloride yield benzylidenebiuret, it was of interest to see if benzal chloride and sulpho-urea would yield the corresponding sulpho-biuret, especially as this body was made by L. Brodsky[1] some years ago in a very different manner, viz., by heating together benzaldehyde and ammonium sulphocyanate. Benzal chloride heated with sulpho-urea reacts violently, the temperature rises rapidly and there is a lively evolution of gas bubbles, the contents of the flask taking on first a yellow, and then a brownish color, and, unless benzal chloride is present in great excess, only a reddish resinous mass is left. After numerous experiments I found the following to be the best method for obtaining a tolerably pure product:

40 grams of dry sulpho-urea and 60 grams of benzal chloride are heated in a flask on a paraffin-bath until the beginning of a

[1] Sitzungsber. der kais. Akad. der Wiss. in Wien. **95**, II Abth. 69.

reaction is observed. At 150° C. the reaction is already so violent that the flask must at once be removed from the bath in order to keep its contents from turning into a resinous by-product. If an excess of benzal chloride has not been taken, and if the temperature has not been watched with the greatest care, it will rise rapidly to 190° C. in spite of the removal of the flask from the paraffin-bath. Reddish-brown vapors, extremely irritating to the mucous membrane, arise in clouds, and, when these cease to be given off, only the unutilisable resin before spoken of remains. On the other hand, when a sufficient quantity of benzal chloride has been taken and the temperature has not been allowed to go above 150° C., a reddish-yellow granular mass is formed, the development of gas is only moderate, and colored vapors do not appear. After cooling, the raw product is recrystallised out of hot water, in which, however, it dissolves with difficulty, and for its complete purification the product thus obtained is several times precipitated from hot alcohol by ether, which causes it to fall in snow-white crystalline flakes. These when dried over sulphuric acid gave on elementary analysis results which correspond with the empirical formula $C_9H_{10}ClN_3S_2$. Determinations of the molecular weight also gave results which speak for this formula. Thus *M* was found to be 251; calculated, 259.

Accordingly we may perhaps regard this body as being formed in agreement with the following equation:

$$C_6H_5.CHCl_2 + 2CS.N_2H_4 = C_9H_{10}ClS_2N_3 + NH_4Cl;$$

and as being chlorbenzylidenethiobiuret. At any rate the benzylidenebiuret of Brodsky is not formed in this reaction. In addition to chlorbenzylidenethiobiuret and ammonium chloride no other bodies were obtained. It is my purpose to determine the constitution of chlorbenzylidenebiuret by repeated analyses of its salts and of its decomposition-products. I may add that by dissolving it in concentrated sulphuric acid or in glacial acetic acid, new and beautifully crystalline chlorine-free products are obtained.

Laboratory of Prof. v. Nencki, Berne, Switzerland.

HYDRATED LEAD OXIDE.

By C. Luedeking.

There seem to be at least two hydrated oxides of lead; $3PbO.H_2O$ obtained by Payen,[1] and $2PbO.H_2O$ prepared by Schaffner.[2] Payen obtained his hydrate in the form of strongly-refracting octahedra by allowing an ammoniacal solution of lead acetate to crystallise in a closed vessel. It is very questionable whether the crystals so obtained are entirely free from basic salt or ammonia. Calvert[3] observed that hydrated oxide of lead can combine with ammonia, and Winkelblech[4] maintains that the hydrated oxide so obtained always contains small amounts of basic salt which cannot be removed by excess of alkali.

Schaffner claims to be able to obtain his hydrated oxide entirely free from basic salt by precipitating a solution of lead acetate with a slight excess of potassium hydrate.

It is possible to obtain the hydrated oxide of lead of Schaffner in excellent crystals in another way, which may form the basis for obtaining from other metals also hydrated oxides soluble in potassium hydrate. When litharge is boiled with a strong solution of potassium hydrate for some time, a considerable amount of it passes into solution. The potassium hydrate solution, when strong, deposits on cooling a large quantity of crystals of anhydrous protoxide of lead, as had been observed by several authors previously. The solution, after it has become perfectly cold, however, still contains a large amount of lead oxide. When now it is exposed in a small beaker to the air, carbon dioxide is slowly absorbed and potassium carbonate formed. Thus the lead is gradually and very slowly deprived of its solvent and all conditions for crystallisation pertain. After several weeks the bottom of the vessel will be found covered with magnificently-developed crystals, perfectly colorless and transparent, and having a high refractive-power for light and brilliant luster. These crystals, on examination, are found to be the hydrate $2PbO.H_2O$ in a state of absolute purity. They belong to the tetragonal system, are simple in development and short and thick in habit, showing the prism $\infty P\infty$, and the pyramid P at either end. The angle between

[1] Ann. chim. phys. [4] **8**, 302.
[2] Ann. Chem. (Liebig) **51**, 175.
[3] Compt. rend. **22**, 480.
[4] Ann. Chem. (Liebig) **21**, 29.

the opposite edges, over the solid angle of the pyramid, is 101°. The axial relations are 1 : 1 : 0.824. Their reaction is alkaline, and on exposure to the air they soon become opaque, absorbing carbon dioxide and forming lead carbonate. In this metamorphosis, however, they maintain sharply their original form. On heating they lose their water and become yellow litharge, but nevertheless maintain the original crystalline form.

The structure of this hydrate is probably the following: $Pb\begin{matrix}OH\\O\\OH\end{matrix}Pb$.

We may consider that it is rather to be expected that the weaker the base the fewer OH-radicals will it contain. Take, for example, calcium hydrate—a much stronger base—and we have all the affinities of calcium saturated with hydroxyl groups.

The less the basic powers of an element, when it can form hydrates, the greater the likelihood of its forming such hydrates as that we have examined, and even others such as $3PbO.H_2O$, which has, in fact, been actually obtained. Thus it will be easy to form from a strong base a hydrated oxide containing the normal number of hydroxyl groups, while for a weak base this will be difficult; and *vice versa*. This will explain in a chemical way what appears at first anomalous and only mechanical admixture, viz., the small amount of water contained in many oxides of the heavier metals.

Chemical Laboratory, Washington University.

ON THE MELTING POINT OF CERTAIN ALLOYS.

By Fred. C. Weld.

In some experiments which I made for practical purposes I had occasion to determine the melting points of several low-melting alloys. In view of the work of Heycock and Neville, it seems worth while to publish the results.

Heycock and Neville[1] find that each atom of the following metals alloyed with 100 atoms of tin reduces the melting point—

[1] Chem. News **59**, 175.

or, in the case of antimony, raises it—as follows: zinc, 2.53°; copper, 2.47°; silver, 2.67°; cadmium, 2.16°; lead, 2.22°; mercury, 2.3°; aluminium, 1.34°; antimony, 2°.

My results show the limit to which this is true in the case of tin and lead:

Melting point of tin (fine bar).		Atoms of lead.		Factor for lead.		Calculated melting point.	Found.
227°	minus	3.28	×	2.22°	=	219.72°	218°–219°
"	"	11.24	×	2.22°	=	202.05°	201.5°
"	"	15.13	×	2.22°	=	193.41°	194°
"	"	17.19	×	2.22°	=	188.84°	193°
"	"	19.47	×	2.22°	=	183.78°	188°–190°
"	"	38.18	×	2.22°	=	142.24°	180°
"	"	57.28	×	2.22°	=	99.84°	180°
"	"	85.12	×	2.22°	=	38.03°	209°

It will be seen from these figures that the rule of Heycock and Neville holds only to 15 atoms of lead in 100 of tin; further, that the lowest melting point possible is obtained from 38 atoms of lead. I am not prepared as yet to advance any theory to account for these phenomena.

The method used was very simple, but gave satisfactory results. The alloys, after being fused and cooled, were again fused and stirred while cooling with an ordinary glass thermometer. Melting points obtained in this manner checked exactly with one made in an ordinary melting-point apparatus. My lower results check within a degree those of Heycock and Neville, and the melting point of the tin is within a degree of that of pure tin (228°).

The effects of this reduction of the melting point are not cumulative, *e. g.*, the melting point of an alloy of 100 atoms of tin and 57.28 atoms of lead is 180°; the melting point of an alloy of 100 atoms of tin, 57.28 atoms of lead and 5.89 atoms of mercury is not $180° - 5.89 \times 2.3° = 166.45°$, but is 173°. So also the calculated melting point for an alloy of 100 atoms of tin, 57.28 atoms of lead and 19.2 atoms of mercury would be 131.23°; the actual melting point is 156°.

The following alloys containing bismuth, for which as yet no factor has been determined, were tested. In the calculated melting point the bismuth has been left entirely out of consideration, although it undoubtedly reduces the melting point. The starting point in the calculation has been 180°, the melting point of an alloy of 57.28 atoms of lead and 100 atoms of tin.

Tin (atoms).	Lead (atoms).	Mercury (atoms).	Zinc (atoms).	Bismuth (atoms).	Calculated.	Found.
100	57.28	12.58	7.04	3.3	133 26°	145°–150°
100	57.28	8.41	...	2.24	160.66°	166°–167°
100	57.28	10.58	13.02	4.03	122.72°	148°
100	57.28	12.82	5.63	2.66	136.27°	145°

THE DETECTION OF CONIINE IN A CASE OF POISONING.

By Launcelot W. Andrews.

Coniine so rarely takes a part in toxicological cases that a brief report of such a case will perhaps possess sufficient interest to warrant publication, more especially since the investigations of recent years concerning ptomaines have so greatly complicated the labors of the toxicologist and increased the chances of escape of the criminal by enabling him to ascribe the observed reactions of an isolated poison to some hypothetical ptomaine. So long as our knowledge of this latter class of bodies is confessedly incomplete, the expert may be confronted with the question, "How do you know that no ptomaine exists which may give all the reactions of the alkaloid you profess to have discovered?" and he will find it a hard one to answer in such a way as to satisfy an average jury.

In the particular case which forms the motive of this article I succeeded in determining the molecular weight of the alkaloid found (coniine) through the analysis of one of its salts, and thus characterised it more positively than would be possible by means of qualitative reactions alone. The demonstration of the feasibility of this method has not, so far as I am aware, previously been offered. I cannot but believe that it is capable of more extended application.[1]

The objects submitted to me for examination in the case of the State of Iowa *v.* V. de V., with instructions to "look for strych-

[1] I do not wish to be understood as saying by this that the amount of substance available would always or even usually be sufficient for a molecular-weight determination, but would emphasise the importance of such a determination when possible.

nine and other poisons," consisted of a jar of soup and a stomach. The latter was, remarkably enough, immersed in a jar of a preservative sold under the name of "bromo-chloralum," which consists mainly of a solution of the chlorides of magnesium and aluminum with a small quantity of bromides.

The ligatures at the ends of the stomach were so indifferently secured that one of them had come off, allowing the contents of the stomach to mix with the preservative solution. The comparatively large quantity of aluminum and magnesium salts soluble in alcohol thus brought of necessity into the analysis was of course troublesome in the examination for alkaloids. The interior of the stomach was coated with a coffee-colored scum or fur. It exhibited near the pyloric end some large inflamed patches and numerous small pin-head dots of intense inflammation. Inspection with a magnifier failed to reveal any foreign substance in connection with these spots.

The examination for inorganic poisons may be passed over, since it revealed nothing abnormal beyond the constituents of the "bromo-chloralum" above mentioned.

In the examination for alkaloids the method of Dragendorff was in the main followed. The stomach (and contents, see above) was examined in several portions.

162 grams cut up fine were digested for some time with pure 96 per cent. alcohol and ten drops of sulphuric acid. The liquid was strained off, the residue washed with alcohol, and filtrate together with washings evaporated at 50° C. to one-third its former bulk.

This solution when cold was strained, filtered and shaken successively with petroleum ether,[1] benzene and chloroform. Each of these solvents after washing with water left upon evaporation amorphous residues, not bitter and not possessing alkaloidal properties. A marked tendency to form emulsions was met by repeated filtrations through absorbent cotton.

The solution was then rendered alkaline with sodium hydrate and filtered.[2] The precipitate was washed with a little alcohol, and a portion of the filtrate together with washings shaken with petroleum ether. The petroleum ether solution after filtration was allowed to evaporate on a watch-glass with a drop of concen-

[1] Previously purified by shaking with concentrated sulphuric acid and by fractional distillation.

[2] The filtrate is designated "B."

trated hydrochloric acid. This turned red and then violet blue.[1] The hydrochloric acid on evaporation left a crystalline residue (needle and dagger forms, etc.), contaminated with dark colored amorphous matter. For further purification it was treated with absolute alcohol, filtered and evaporated. This residue was colorless and crystallised in needles.

With this substance the following reactions were obtained: With phosphomolybdic acid, pale yellow amorphous precipitate. With potassio-mercuric iodide, the same. With mercuric iodide, white amorphous precipitate. With gold chloride, pale yellow micro-crystalline precipitate. With concentrated sulphuric acid and potassium dichromate, no coloration except from gradual reduction of chromic acid. With picric acid, no change.[2] With platinic chloride, no change. With potassium bichromate, no precipitate. With iodine in potassium iodide solution, brown precipitate, which disappears and is reproduced upon further addition of the reagent.

The rest of the solution mentioned above and designated "B" was then in part shaken with chloroform, in part with ether ("C"). From the former was obtained with hydrochloric acid a mass of trabecular crystals indistinguishable from coniine hydrochloride, of which a specimen for direct comparison was prepared by recrystallisation under similar conditions from a sample of Merck's.

This preparation exhibited under the polarising microscope the well-known play of colors. It weighed 1.0 milligram, and was utilised for a physiological test. For this purpose it was dissolved in a small quantity of water and administered hypodermically to a cat. Great dilation of the pupils ensued, and they did not contract when exposed to the light of a burning magnesium ribbon. The animal's nose turned blue, violent trembling followed and continued for a long time. The respiration became labored and irregular, the hind legs weak or partially paralysed, then a nearly-complete torpor set in, followed by recovery in four hours.

[1] Reaction of imperfectly purified coniine. (Dragendorff: "Gerichtlich-chemische Ermittelung von Giften," 2d ed., p. 248.)

[2] Ibid. p. 132. Wormley states that an alcoholic solution of picric acid precipitates coniine from "aqueous solutions," an observation which I cannot confirm. The drawing which he gives of crystals of coniine picrate bears a remarkably close resemblance to crystals of picric acid such as may be obtained by adding an alcoholic solution of picric acid to water. (Vide Micro-chemistry of Poisons, page 451 and plates.)

The ether solution ("C") evolved a distinct odor of coniine. On treatment with hydrochloric acid and evaporation it left a crystalline residue identical with that already described, and which with a drop of sodium hydrate solution emitted an intense coniine odor, microscopic oily globules forming in the drop at the same time. This hydrochloride, in addition to the reactions obtained with the previous preparations, on solution in water and treatment with a solution of bromine in hydrobromic acid, gave a magma of felted crystals intermingled with orange oily droplets.

A further portion of the stomach, etc., weighing 135 grams was worked up with an especial view to isolating, if possible, a sufficient quantity of the alkaloidal hydrochloride above described for a quantitative determination of the hydrochloric acid. The material was digested with its own weight of alcohol and ten drops of sulphuric acid for ten hours, then strained and the residue exhausted with alcohol. The united solutions, after distillation to one-third of original volume, were strained, filtered and evaporated at a low temperature under reduced pressure to the consistency of a viscid syrup. This was thoroughly mixed with about six volumes of absolute alcohol, filtered, evaporated as before to a thick syrup, dissolved in a small quantity of water and filtered. This liquid was washed by shaking once with chloroform. Then it was made alkaline with sodium carbonate and shaken with chloroform. The whole mass became at this point a pasty emulsion smelling of coniine. It was stirred up with some freshly ignited asbestos fiber and filtered with the aid of a vacuum pump, the precipitate being washed with a few drops of absolute alcohol and chloroform. The filtrate was carefully treated with a slight excess of sodium hydrate, which produced a fresh precipitate (consisting of magnesium hydrate). It was again shaken with the same chloroform and again filtered. The chloroform now separated readily from the aqueous layer.

The latter was exhausted of alkaloid by successive shakings with small quantities of chloroform. These chloroform solutions were one by one well shaken with about 10 cc. of normal hydrochloric acid until the test with iodine solution showed that they had parted with all their alkaloid. The colorless hydrochloric acid solution was made alkaline with sodium hydrate, and twice shaken with three times its volume of chloroform. The latter was drawn off, filtered clear, and exposed *in vacuo* over sulphuric acid

until its volume was reduced to about 15 cc. (removal of ammonia). It was then treated with hydrochloric acid gas, which caused turpidity and the separation of colorless acicular crystals. It was then allowed to evaporate *in vacuo* in contact with two drops of concentrated hydrochloric acid. The crystalline residuum exhibited crystals of two kinds, viz. ammonium chloride and coniine hydrochloride. On treatment with absolute alcohol the latter dissolved. The filtered alcoholic solution, after evaporation, left a trabecular mass of crystals showing a superb play of colors when examined in polarised light. Crystals of ammonium chloride could not be detected with the polarising microscope in this preparation, which appeared entirely homogeneous.

The weight of the crystals was .0102 gram. They were dissolved in water, and the hydrochloric acid in them titrated by Mohr's method with $\frac{3}{100}$ normal silver nitrate. The burette employed was of very narrow caliber and divided into $\frac{1}{50}$ cc., being easily read to $\frac{1}{100}$ cc.

Required 2.10 cc. $\frac{3}{100}$ normal silver nitrate solution = 2.293 milligrams HCl found = 22.48 per cent. HCl.

Calculated for coniine hydrochloride, $C_8H_{17}NHCl$, 22.28 per cent.

Molecular weight of base, found, 125.4.

Molecular weight of coniine, calculated, 126.8.

It will be unnecessary to describe in detail the detection of coniine in the soup of which the deceased had partaken four hours before her death. The methods employed were essentially the same as those already described, and the results were identical, except that the observed reactions indicated the presence of a relatively much larger amount of coniine, which was unmistakably identified by all its reactions specified above, and by the well known characteristic behavior of its saturated aqueous solution when alternately warmed and cooled.[1]

All the solvents used in this investigation were run through parallel blank tests, which established their purity as regards substances of alkaloidal reaction.

It is with confidence that I submit to the judgment of the profession at large the claim made by the defense that the alkaloid isolated by me and identified as coniine was in reality an unnamed ptomaine.

[1] Beilstein: Organische Chemie, 2nd Ed., **3**, 627.

This assertion will be estimated at its true value when it is remembered, in addition to the direct evidence, that the stomach and the soup had been subjected to entirely different conditions, that they constituted perfectly distinct "nutrient media." Under these circumstances the unsupported assumption that in both objects precisely the same ptomaine should have been generated lacks rational basis.

CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA.

THE DISSOCIATION OF MAGNESIUM OXIDE BY MEANS OF METALLIC MAGNESIUM.

BY H. N. MORSE AND J. WHITE, JR.

In former papers[1] we have described the dissociation which takes place when the oxides or sulphides of zinc and cadmium are heated in a vacuum with their respective metals. Since then we have found that the oxide of magnesium undergoes an equally unmistakable dissociation when it is heated in the same way with metallic magnesium.

The apparatus which we employed was essentially the same as that used in the dissociation of the oxides and sulphides of zinc and cadmium, except that, owing to the energetic action of the vapors of magnesium on silicates, it was found advantageous to inclose the mixture of oxide and metal in a tube of sheet-iron. The iron tube was made by forming a thoroughly-cleansed strip of the metal, from 40 to 45 centimeters long, around an iron rod of proper thickness, and closing one end with the hammer. It was then prepared for use by inclosing it in a glass tube, exhausting with the Sprengel pump, and heating to redness until it ceased to give off volatile matter.

Owing to the presence of considerable quantities of occluded hydrogen in commercial magnesium, as observed by Dumas,[2] the metal was distilled in a vacuum in the manner described by Burton and Vorce.[3] The oxide of magnesium, also, was heated to redness in a vacuum until it ceased to give off carbon dioxide.

[1] This Journal **11**, 258 and 348. [2] Compt. rend. **90**, 1027.
[3] This Journal **12**, 219.

The metal and then the oxide were dropped into the iron tube. This was then placed in a larger tube of hard glass which had been closed at one end. The length of the glass tube was usually about 80 centimeters, or twice that of the iron tube. The outer tube was then drawn out at the open end, attached to the Sprengel pump, exhausted, and finally heated in a combustion furnace along that portion which was occupied by the iron tube. The quantities of magnesium employed in our experiments varied from 4.5 to 10 grams; those of the oxide, from 1.5 to 3 grams.

In every case the phenomena which presented themselves when the tube had reached a bright red heat were similar to those observed when the oxides of zinc and cadmium were heated with their metals. The oxide formed in the cool portion of the glass tube, and fell upon the bottom in a long line which extended even into the connecting tube of the pump itself. This transportation of the oxide continued until the greater portion of the metal had distilled to and condensed about the open end of the iron tube. At the same time gas was evolved and collected in the eudiometer placed over the outlet of the pump. This gas proved to be a mixture of carbon dioxide and free oxygen. The proportion of the oxide thus transported to the cooler portion of the glass tube was quite variable, and appeared to depend on the thoroughness with which the oxide and metal were mingled in the iron tube. It was always found to be greater when the mixture of oxide and metal which remained in the inner tube after one experiment was reheated with an additional quantity of magnesium. It was not possible to determine the exact amount of oxide which was carried out of the iron tube, owing to the presence in it of some distilled metal; but on several occasions that portion of the oxide which was nearest the pump and appeared to be free from metal was collected and weighed. The quantity varied from 0.1 gram to 1.5 gram. In some cases only a small fraction of the oxide remained in the iron tube.

As in the case of the oxides of zinc and cadmium, the evolution of oxygen was most rapid during early stages of the experiment, before the tube had become filled with the vapors of the metal. The carbon dioxide, which must have come from the carbon contained in the iron, was removed by caustic potash, and the oxygen determined by means of an alkaline solution of pyrogallic acid. The quantity of oxygen found varied from 1.5 to 3 cc.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.

ANALYSIS OF MILK OF RIPE AND UNRIPE COCOANUTS.

By Lucius L. Van Slyke.

As a member of the U. S. Yellow Fever Commission, Dr. Geo. M. Sternberg, during a residence in Cuba for the purpose of investigating the yellow fever, made use of the milk of unripe cocoanuts as a culture medium for studying certain bacteria. In order to ascertain the composition of the milk so used, Dr. Sternberg procured six unripe cocoanuts from Cuba and placed them in my hands for analysis.

What is known as the meat of the cocoanut had in each of these six nuts just begun to form, covering the inside of the shell with a very thin, soft, nearly transparent layer.

So far as I have been able to ascertain, there is not on record any analysis of the milk of the cocoanut at this stage of growth. Hammerbacher has published an analysis of the mixed milk of two cocoanuts, which were presumably ripe, like those ordinarily obtained in the market. For purpose of comparison, I also made an analysis of the milk of one ripe cocoanut.

The milk of the unripe nuts was transparent like water, containing in suspension small amounts of a cloudy-white substance which was readily removed by filtration. In the ripe nut, the milk was quite turbid in appearance and did not filter clear.

Following is a brief explanation of the methods employed in making some of the determinations:

1. A picnometer was used for determining specific gravity, careful attention being given to temperature.

2. The water was determined by heating a weighed portion at 60° C. to constant weight. A temperature much above this causes dehydration of the glucose and a correspondingly increased percentage of water.

3. In determining the amount of albuminoids, about 60 grams of milk were evaporated to a small bulk and the nitrogen determined according to the Kjeldahl process as modified by Gunning. The amount of nitrogen thus obtained was multiplied by the factor 6.25 to determine the amount of albuminoids.

The following table gives the results of the different analyses, including those of Hammerbacher's analysis:

Analysis of Milk of Cocoanuts.	Milk of Unripe Cocoanuts.						Milk of Ripe Cocoanut.	Hammerlacher's Analysis.
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
Weight, in grams	230.5	378.6	347.	383.7	350.	330.	109 6	151.9
Specific Gravity, at 15.5° C.	1.0246	1.023	1.0223	1.023	1.0221	1.0215	1.044	1.0442
Water, per cent., at 60° C.	94.37	94.48	94 59	94.89	95 27	96.43	91.23	91.50
Ash, per cent.	0.575	0.635	0.675	0.611	0.608	0.602	1.06	1.19
Glucose, per cent.	4.58	3.83	3.45	4.06	4.36	3.56	Trace	....
Cane Sugar, per cent.	Trace	Trace	Trace	Trace	Trace	Trace	4.42	....
Albuminoids, per cent.	0.120	0.126	0.114	0.205	0.140	0.095	0.291	0.46
Fat, per ct. (Ether extract)	0.084	0.100	0.138	0.131	0.145	0.120	0.145	0.07

Briefly comparing the results given in the foregoing table, we notice that the milk of the ripe cocoanut differs from that of the unripe cocoanut in the following particulars:

The former is, first, less in amount in each nut; second, greater in specific gravity; third, contains less water; fourth, contains more ash and albuminoids; and fifth, contains cane sugar with traces of glucose, the opposite being true in case of the milk of the unripe nut, which contains glucose with traces of cane sugar.

Chemical Laboratory, Johns Hopkins University.

REVIEWS AND REPORTS.

Recent Progress in Industrial Chemistry.

III.—*Chlorates, Electrolysis, and Potassium Salts.*

Chlorates.—The ordinary process for the manufacture of potassium chlorate consists, as is well known, in passing chlorine into milk of lime, forming a solution of calcium chlorate and chloride, then decomposing the chlorate by the addition of an equivalent

quantity of potassium chloride, and crystallising out the potassium chlorate formed. Theoretically, the action of chlorine on lime should give five equivalents of chloride to one of chlorate; practically, nearly six equivalents of chloride are obtained. It is impossible to separate the potassium chlorate completely from the large amount of calcium chloride by crystallisation, and under ordinary circumstances about twenty per cent. of the product is lost in the mother-liquors. Hammill[1] finds that this loss can be greatly reduced by diluting the liquor slightly and lowering its temperature to 0° C. by refrigerating apparatus. By this method the yield of chlorate is said to be increased one-seventh, and the loss is reduced to nine or ten per cent.

A further modification of the old method is the process of Muspratt and Eschellmann, in which magnesia instead of lime is suspended in water and saturated with chlorine. Magnesium chloride and chlorate are produced in about the same proportion as the corresponding calcium compounds; by evaporation, however, one-half the magnesium chloride may be crystallised out, thus making it possible, after the addition of the potassium chloride, to separate the chlorate far more completely than in the ordinary process. The magnesium chloride obtained in large quantity as a by-product is sold for use in the sizing of cotton. This method is in use at the works of James Muspratt & Sons, Widnes, England.

The process of the future for the manufacture of chlorates appears, however, to be a combination of the above with the Weldon-Pechiney chlorine process. This is now being worked experimentally in France and England. Magnesia is suspended in water and saturated with chlorine, producing chloride and chlorate. Potassium chloride is added, forming potassium chlorate and magnesium chloride. After crystallising out the chlorate the solution is evaporated with the addition of magnesia, and the oxychloride thus formed heated in a current of air, forming chlorine and magnesia, as in the Weldon-Pechiney process. Thus both the magnesia and the chlorine are regained. Theoretically, this method will yield potassium chlorate *without consumption of chlorine*, by the combination of potassium chloride, through the agency of magnesia, with the oxygen of the air. The only apparent obstacle to the success of this remarkable process is the dense character of the magnesia resulting from the calcination of the oxychloride in a current of air at the high temperature necessary to liberate the chlorine. Such magnesia is but slowly acted upon by chlorine. Whether this obstacle can be overcome time alone will show.

Sodium chlorate has come into extensive use during the past few years as an oxidising agent in dyeing by means of aniline-black. For this purpose potassium chlorate is not sufficiently

[1] J. Soc. Chem. Ind., 1889, p. 524.

soluble. Owing to the difficulty of separating the very soluble sodium chlorate from solutions of sodium or calcium chlorides, this salt has until very lately been made at great expense from the potassium compound. Pechiney has, however, solved the problem of the industrial preparation of sodium chlorate; his process, now carried on extensively at his works at Salindres, France, is as follows:[1] Chlorine is passed into milk of lime, as usual, producing "chlorate liquor," containing five and one-half equivalents of chloride to one of chlorate. The liquor is then submitted to refrigeration, and at a temperature of 10° to 12° C. most of the calcium chloride crystallises out as the hydrated salt $CaCl_2.2H_2O$. By addition of lime to the liquor, and heating to 80° C., nearly all the remaining chloride is precipitated as oxychloride, and the resulting solution, after filtration, contains only three-tenths of one equivalent of chloride to one of chlorate. To this sodium sulphate is added, precipitating calcium sulphate and forming sodium chlorate; by evaporation this is obtained in well-formed cubical crystals, and is now sold at a price but little above that of the potassium salt.

Within the past two years potassium chlorate has been successfully manufactured by electrolysis. An account of the process will be found below.

The Application of Electrolysis in Chemical Industry.—Electrometallurgy, or the separation of metals from their compounds by means of electricity, has long been practiced. In this way, early in the century, Davy first isolated potassium, sodium, lithium, calcium, and other metals. In modern times electric methods have been successfully applied in the separation and purification of the more common metals, especially zinc and copper, while electro-plating with various metals has become one of the commonest industries. With the development of modern dynamo-electric machines the cost of producing powerful currents of electricity has been enormously reduced, and new industrial applications of this force have quickly followed. Two metals, magnesium and aluminum, formerly reduced at high cost by means of sodium, are now cheaply obtained by electrolysis. Graetzel's electric process for the preparation of magnesium is now carried out on a large scale near Bremen, and the cheap metal so produced has supplanted that formerly obtained at Manchester and Boston by the old process of Caron and Deville. Within the past two years a company at Pittsburgh has succeeded in producing metallic aluminum at low cost by the electrolysis of fused cryolite, and is now manufacturing the metal on a considerable scale.

Many proposals have been made for decomposing common salt by an electric current, but the great power required and low price of the products obtained have heretofore made the industrial

[1] Weldon: J. Soc. Chem. Ind., 1882, p. 41.

application of the process quite hopeless. The subject of the electrolysis of chlorides has, however, received careful study of late, and it will perhaps be of interest to examine briefly the present aspect of this important question.

The first effect of the electrolysis of sodium chloride is, of course, the separation of sodium at the negative pole and the liberation of chlorine at the positive. If the action takes place in solution, however, the sodium set free will decompose the water present, forming sodium hydroxide and liberating hydrogen; if the electrodes are separated by a porous diaphragm, therefore, chlorine will be set free at the positive pole, while at the negative pole hydrogen will be given off and caustic soda will remain in solution. On the other hand, if the porous diaphragm is absent, the chlorine will react on the caustic soda, forming sodium chloride and sodium chlorate or hypochlorite, according to the temperature and strength of the solution.

The question of the power required for the decomposition of salt by electricity has lately been discussed in an interesting paper by Hempel.[1] His apparatus consisted of a cell divided by a porous partition of asbestos paper clamped between perforated electrodes, one of carbon and the other of sheet iron. The cell was filled with a solution of salt, which was kept saturated by automatic addition of dry salt. By the action of the current nearly pure chlorine was liberated at the carbon pole, while the opposite division of the cell became filled with a strong solution of caustic soda. A constant stream of carbon dioxide was passed into this solution, forming sodium carbonate, which was deposited in crystals and from time to time removed. The process was thus made continuous. Hempel found that one horse-power (calculated as equivalent to 680 volt-ampères) yielded 64.5 grams of chlorine and 259.8 grams of crystallised sodium carbonate ($Na_2CO_3 + 10H_2O$) per hour. From this, assuming that equally good results could be obtained on a large scale, and calculating the alkali as soda-ash, we have:

1 h. p. = 1548 grams chlorine (= 3.41 lbs.), and 2308.8 grams soda-ash (= 5.09 lbs.) per day of 24 hours, or 586 h. p. = 1 ton chlorine and 1½ tons soda-ash per day. With coal at $2.50 per ton, the cost of producing this power would be about 12 cents per h. p. per day, or, for 586 h. p., $70.32 per day.

If one ton of chlorine is calculated as equivalent to three tons bleaching powder, the value of the products, at the present market rates in this country (soda-ash, $30, and bleaching powder, $35 per ton), would be about $150, or more than twice the cost of the power. A liberal allowance must, however, be made for the expenses of the process and interest on the cost of plant, and it is not probable that the industry would prove remunerative unless a much cheaper source of power than steam can be made available.

[1] Ber. d. chem. Ges. 22, 2475.

It is not impossible that the use of very cheap fuel or water-power may make the electrolysis of salt practicable on a large scale.

In the case of potassium chloride, however, the conditions are much more favorable. Over 80,000 tons of this salt were produced at Stassfurt in 1889. A large part of this is converted by the Leblanc process into potassium carbonate, with the production of over 25,000 tons per year. The value of potash is at least five times that of soda ash, while the decomposition of potassium chloride by electrolysis is more easily accomplished than that of salt. Within the past year the electrolytic potash-process has been perfected, and is now in successful operation at Griessheim, near Frankfort. The power employed amounts to 1000 horse-power, and is generated by means of steam, using coal as fuel. There is reason to believe that this may be the process of the future for the production of potash from the chloride.

The subject of the electrolysis of chlorides without the use of a porous diaphragm, resulting in the formation of hypochlorite and chlorate as already explained, has received increased attention since the introduction of the *Hermite electric bleaching process*, patented in France, England and other countries in 1885. In this process a bleaching liquor is produced by the electrolysis of a solution of magnesium chloride. The apparatus consists of a trough containing the solution; the positive electrodes, consisting of a series of ebonite frames carrying sheets of platinum wire gauze, alternate with the negative electrodes formed of circular plates of zinc. The latter are kept in constant revolution, and any deposit which may become attached to them is removed by an ebonite knife bearing against each plate. The effect of the electrolysis is to produce a certain amount of magnesium hypochlorite. The solution is used directly for bleaching purposes, and re-electrolysed when its bleaching effect becomes feeble. The process has been introduced in a number of works in Europe, and also at two important manufactories near Boston; its chief use is the bleaching of wood-pulp in paper manufacture. The Hermite Company, in their Paris Exposition circular, offer to guarantee the production, every 24 hours, with nine horse-power and a current of 1000 ampères, of bleaching solution equal in efficiency to 100 kilos. of bleaching powder. Assuming 15 cents per horse-power as the cost of this power in a large plant, this claim is equivalent to that of the production of bleaching powder at $13.50 per ton, or about one-third of its present price. The process has been severely criticised by Hurter, who carefully studied the whole subject of the electrolysis of magnesium chloride. He disputes the claims made by the advocates of the process, and shows that beyond a certain point very little hypochlorite is produced, the effect of the current after that being chiefly to produce chlorate and perchlorate. Hurter found that even in the production of a weak bleaching solution containing

two and a half grams of available chlorine per liter, only 20 per cent. of the current was effectively utilised.

Another important application of electrolysis, and one which offers good prospect of success, is the production of *potassium chlorate.* A process with this object has been perfected at Villers-sur-Hermes (Oise), France, by H. Gall and A. de Montlaur. As described in the patent, the process consists in submitting a solution of potassium chloride to electrolysis in a trough divided by a porous partition; the solution is caused to circulate between the two divisions of the cell in such a manner that the products of electrolysis react upon each other. The solution is kept at a temperature of 50°, in order to convert the hypochlorite formed into chlorate. Crystallised potassium chlorate produced by this process was exhibited at the Paris Exposition of 1889. It is stated that the inventors have secured a water-power equal to 1000 horse-power at Vallorbe, Switzerland, and are there erecting a large plant. The current employed is equal to 1000 ampères and 25 volts. One horse-power (requiring 25 kilos. of coal, if generated by steam) yields 1 kilo. of chlorate per day of 24 hours. If these statements are correct, and we assume 15 cents per horse-power per day as the cost of the power, this would correspond to 15 cents per kilo. of chlorate, or considerably below the present market price. With cheap water-power, therefore, there is every reason to believe that the process will be practically successful.

Potassium Salts.—Practically the whole of the world's supply of potassium salts is obtained from the following sources:

1. Leaching of wood-ashes.
2. The suint of sheep-wool.
3. The "vinasses" of the beet-sugar industry.
4. The Stassfurt salt-deposits.

From the first three sources, potash is obtained in the form of carbonate; from the Stassfurt deposits, in which it occurs as carnallite, or the double chloride of potassium and magnesium, the potash is obtained as chloride.

Owing to the rapid disappearance of the forests, the production of potash from wood-ashes, formerly extensively carried on in the United States, Canada, and several countries of Europe, has greatly decreased within the past few years, and is now insignificant in comparison with that from the last two sources mentioned. It is estimated that about 1750 tons of potash were produced from wood-ashes in the United States in 1887.

The production from the suint of sheep-wool is also comparatively unimportant, probably amounting to less than 1000 tons yearly, and is carried on chiefly in the wool-growing districts of France and Belgium. The potash is contained in the suint in the form of the salt of fatty acids, and constitutes nearly one-third the weight of the raw wool. The washings are evaporated and the

residue distilled in retorts, the ammonia and gases given off being utilised. Potash is obtained by leaching the carbonaceous residue left in the retorts.

The extraction of potash from the beet-root residues has been of great importance in the past, especially before the development of the Stassfurt deposits, and is still an industry of considerable magnitude. It is estimated that about 15,000 tons of potash are manufactured yearly from beet-root residues; chiefly in France and Germany. The industry is, however, not increasing, since the new processes for the extraction of crystalline sugar from the molasses (osmose and elution) yield the inorganic salts in a form better adapted to be returned to the soil as fertiliser. Before these processes were introduced the uncrystallisable beet-root molasses was universally submitted to fermentation for the manufacture of alcohol. After distilling off the alcohol so produced, the "vinasses" remaining, containing potash, ammonia salts, and various organic substances, were evaporated to dryness and calcined in open pans. By this method the volatile nitrogenous by-products were wholly lost. A great improvement in this process was introduced by Vincent, and is now employed on a large scale at Courrieres (Pas de Calais), France. This consists in distilling the residue from the evaporation of the vinasses in closed retorts. The volatile products, consisting of trimethylamine, ammonia, methyl alcohol, pyridine bases, etc., are condensed and purified. On repeated distillation, trimethylamine chloride breaks up into ammonia and methyl chloride. The latter is condensed into metal cylinders by pressure, and is now largely used in surgery to produce local anesthesia by the cold of its evaporation, and is also employed in the manufacture of coal-tar colors.

The crude potash remaining in the retorts after calcination contains about 32 per cent. of potassium carbonate, 13 per cent. of chloride, 18 per cent. of sulphate, and 12 per cent. of sodium carbonate.

The production of potassium salts from the Stassfurt deposits continues to increase, and this source now furnishes far more than all others. The total sales of crude potassium chloride at Stassfurt in 1889 amounted to 1,471,000 centners (1 centner = 110.2 lbs. av.) or 81,052 tons. Of this enormous quantity, it is estimated that 41.2 per cent. is consumed in the manufacture of nitrate by treatment with crude Chili saltpetre; 24.2 per cent. is converted into carbonate, chiefly by the Leblanc process; 20.4 per cent. is employed in agriculture, and 7.1 per cent. in the manufacture of bichromate and other salts of potassium.

The conversion of the potassium chloride of Stassfurt into carbonate is now almost universally accomplished by the Leblanc process. The industry was first established at Kalk, near Cologne, in 1863, and is now extensively carried on at that place, and also near Magdeburg and at Stassfurt, with a total

production of over 25,000 tons potassium carbonate per year. The decomposition of the chloride by sulphuric acid is accomplished in open roasters, similar to those formerly employed in the salt-cake process; the Mactear rotary furnaces are also successfully used. Revolving furnaces are employed for the conversion of the sulphate into carbonate, and the operations of leaching and calcination are similar to those followed in the soda industry. Potassium ferrocyanide is obtained from the mother-liquors as a by-product, and amounts to 1 per cent. of the potash produced.

Many attempts have been made to adapt the ammonia-soda process to the manufacture of potassium carbonate, but so far with slight success. Owing to the great solubility of potassium bicarbonate in a solution of ammonium chloride, potassium chloride cannot be treated in the same manner as salt. The use of trimethylamine in place of ammonia allows the precipitation of the potash as bicarbonate, but the *trimethylamine process*, which was tried on a commercial scale at Croix with good prospects of success, has lately been given up. It is said that the process has since been taken up experimentally by the Solvays at some of their works.

The Engel process, which also raised great expectations, consists in passing carbon dioxide into a solution of potassium chloride holding magnesia in suspension. A double carbonate of potassium and magnesium is precipitated, and magnesium chloride left in the solution. The double carbonate is decomposed by boiling with water, precipitating the magnesia as carbonate, while pure potassium carbonate, free from soda, is obtained by evaporating the solution. The magnesium chloride formed is discarded, and the magnesia required supplied in the form of calcined magnesite. The process was tried at Havre and at Stassfurt, but proved a failure from a commercial point of view. An improvement upon this method is said to be that of Borsche and Brünjes, in which ammonia and carbon dioxide are caused to react upon magnesia, and the resulting precipitate of ammonium-magnesium carbonate decomposed with potassium chloride. The Vereinigte Chemischen Fabriken at Stassfurt have recently begun the installation of this process on a large scale, but no information in regard to its practical working has yet been made public.

As stated under the head of "Electrolysis," the electric decomposition of potassium chloride is now being worked on a commercial scale near Frankfort, and there is good reason to expect that this method will play an important part in the potash industry.

Much valuable information in regard to the details of the various processes of manufacture of potassium salts is to be found in a work of Pfeiffer—*Die Kali-industrie:* Braunschweig, 1888.

SPENCER B. NEWBURY.

GRUNDLAGEN DER CHEMIE. Von D. MENDELEJEFF, Professor an der Universität in St. Petersburg. Aus dem Russischen übersetzt von L. JAWEIN, Docent am Technologischen Institut in St. Petersburg, und A. THILLOT, Assistent am chemischen Laboratorium des Technologischen Instituts in St. Petersburg. Carl Ricker, St. Petersburg, 1890.

Chemists are always glad to listen when Professor Mendelejeff speaks,—if he does not speak in his native language. The existence of a work on general chemistry, written by him in Russian, has been almost an aggravation to his admirers, and there has been, it may safely be asserted, a general desire to know what is in the work. Through this translation into German, and one into English already announced, we have it in our power to find out. The first number contains 144 pages, and the publishers announce that the book will be completed in eight numbers, to be issued in rapid succession at the price of three marks each. A table of contents of the entire work is given in lieu of a preface. This table is as follows:

Introduction.—Chapter I. Water and its Compounds.—Chapter II. Composition of Water. Hydrogen.—Chapter III. Oxygen and its Salt-forming Compounds.—Chapter IV. Ozone and Hydrogen peroxide. Dalton's Law.—Chapter V. Nitrogen and Air.—Chapter VI. Compounds of Nitrogen with Hydrogen and Oxygen.—Chapter VII. Molecules and Atoms.—Chapter VIII. Carbon and Hydrocarbons.—Chapter IX. Compounds of Carbon with Oxygen.—Chapter X. Sodium Chloride. Berthelot's Doctrine. Hydrochloric Acid.—Chapter XI. The Halogens: Chlorine, Bromine, Iodine, and Fluorine.—Chapter XII. Sodium. —Chapter XIII. Potassium, Rubidium, Cäsium, and Lithium. Spectroscopic Investigations. — Chapter XIV. Valency and Specific Heat of the Metals. Magnesium, Calcium, Strontium, Barium, and Beryllium.—Chapter XV. The Periodic Law of the Elements. — Chapter XVI. Zinc, Cadmium, and Mercury.— Chapter XVII. Boron, Aluminium and analogous Elements of the Third Group.—Chapter XVIII. Silicon and other Elements of the Fourth Group.— Chapter XIX. Phosphorus and other Elements of the Fifth Group.—Chapter XX. Sulphur, Selenium, and Tellurium.—Chapter XXI. Chromium, Molybdenum, Tungsten, Uranium, and Manganese.—Chapter XXII. Iron, Cobalt, and Nickel.—Chapter XXIII. Platinum Metals.—Chapter XXIV. Copper, Silver, and Gold.—Table of Atomic Weights.—Classification of the Elements into Groups.

The first number carries us through the Introduction, Chapter I, and a few pages of Chapter II. A careful reading of this number shows that the book is one of unusual interest and importance, as we had a full right to expect. There is thought in every line, and there is nothing chemistry is more in need of than clear thought. The author's mind is indeed so full of thoughts that he cannot find room for them in the text, and foot-notes abound to such an extent that considerably more than half the

matter is presented in this form, somewhat, it must be confessed, to the confusion of the reader. The book begins, for example, with these words: "Die Chemie beschäftigt sich mit der Erforschung homogener Stoffe, aus denen alle Körper der Welt zusammengesetzt sind." To these words are appended two long foot-notes in small type, covering nearly two full pages. One of these notes treats of the subject "Erforschung" and the other of "Stoffe" in a philosophical way. On the next page follow notes on "Körper," "Erscheinung," "Reaktion," "Chemische Erscheinung." This method of treatment is characteristic of the book. Under ordinary circumstances one would be disposed to complain, but, as the notes are, for the most part, of great interest and treat of important subjects in a clear, logical way, the inclination to complain gives way to a feeling of thankfulness that the notes have been written.

In these days when the physical side of chemical phenomena is receiving so much attention, the following words of Professor Mendelejeff will be read with special interest: "Die Natur der chemischen Kräfte ist für uns bis jetzt ebenso verborgen, wie die Natur der allgemeinen Schwere, aber auch ohne die Kenntniss derselben konnten, auf Grund mechanischer Begriffe die astronomischen Erscheinungen nicht nur unter ein einheitliches Prinzip gebracht, sondern auch in vielen Einzelheiten vorausgesagt werden; ebenso können auch in der Erforschung der chemischen Erscheinungen, ohne dass das Wesen der chemischen Verwandschaft erkannt wird, dennoch, unter Anwendung der Gesetze der Mechanik, Dank der Fortschritten der mechanischen Wärmetheorie, bedeutende Erfolge erreicht werden. Bis jetzt ist dieser Theil der Chemie noch wenig ausgearbeitet und bildet, als nächste Aufgabe der Wissenschaft, ein besonderes Gebiet, das man theoretische oder physikalische Chemie, am richtigsten *Chemische Mechanik*, nennt. Das Studium dieses Theiles der Chemie setzt die Kenntniss der verschiedenen bis jetzt erhaltenen homogenen Körper, iher chemischen Umwandlungen und der sie begleitenden (thermischen und anderen) Erscheinungen voraus. Zweck des vorliegenden Werkes ist eben den Anfänger mit diesen chemischen Grundbegriffen vertraut zu machen." In a foot-note the author then states that in this book he will present only a few general conceptions of chemical mechanics. He says further: "Wie die Erfolge der Chemie zu Lavoisier's Zeiten einen fördernden Einfluss auf die gesammte Naturforschung ausgeübt haben, so muss, meiner Ansicht nach, eine selbständige chemische Mechanik neues Licht auf die gesammte molekulare Mechanik werfen, die als die Hauptaufgabe der modernen exakten Wissenschaft anzusehen ist."

In the chapter on water and its compounds there are extensive notes on *Dalton's law*, *the measurement of gas volumes*, *river water*, *potable waters*, *mineral waters*, *sea water*, *specific heat of water*, *dialysis*, and *solution*. The subject of solution is very fully

treated, nearly sixty pages of text and notes being given to this and the allied subjects, *water of crystallisation*, *cryohydrates*, and *hydrates*. As is well known, the author regards solutions as definite, liquid, chemical compounds in a state of dissociation, a conception which differs from that of Arrhenius as well as from that of Pickering. But he justifies his position by strong arguments based upon experiment, and it is certain that no one can deal with the subject of solution without taking into serious consideration the facts established by Mendelejeff.

Every teacher and every advanced student of chemistry should read and study this book with care. Even the most experienced teacher will find much in it that will prove of value to him.

I. R.

CHEMICAL ARITHMETIC, Part I. A Collection of Tables, Mathematical, Chemical and Physical, for the Use of Chemists and others. By W. DITTMAR, LL. D., F. R. SS. Glasgow: William Hodge & Co., 1890. xvi + 175 pp. 8vo.

In the preface the author says: "The general idea by which I have been guided in its compilation is to try to offer to the scientific, as well as the technical, chemist a fairly complete collection of what he needs of mathematical auxiliaries and of chemical and physical constants in the ordinary routine of his laboratory work, and that *without going further*. This book, accordingly, does not pretend to compete with works of the order of Clarke's 'Constants of Nature,' or even of Landolt and Börnstein's 'Tabellen,' nor is it intended to supplant books which, like Lunge and Hurter's 'Pocket-Book,' address themselves to specialists in this or that branch of technical chemistry."

The book is evidently prepared with great care, and is arranged in a convenient form. There are four tables of logarithms, one of which, carried out to five places, is indexed to assist ready reference. Following these are tables giving the atomic weights of elements and the molecular weights of compounds, with the corresponding logarithms; analytical factors and their logarithms; factors used in the calculation of gas volumes; specific gravity tables; thermometer-correction formulae, etc. Almost every calculation which the average student of chemistry would be called on to make is here furnished. Nevertheless the special value of this work seems to lie rather in its accuracy than in its fulness. The paper and press-work are unusually good.

W. W. R.

A TECHNOLOGICAL DICTIONARY OF INSURANCE CHEMISTRY. By WM. A. HARRIS. Liverpool: The Author, 1890. xi + 407 pp. 12mo.

This book takes up for discussion in alphabetical order all ordinary natural and artificial products, and especially the methods of

manufacture, of transportation and of storage employed, as well as the results of changes of temperature, etc., upon them, the object being to show in what respect these matters concern fire insurance companies. Such substances and mixtures of substances as are liable to what is ordinarily called "spontaneous combustion" are treated of with much detail. The transportation of fire by means of mill-dust, coal-dust, and the vapors of hydrocarbons, etc., is also discussed at length. The dangers attendant upon the transportation and storage of carelessly-packed cotton, hay, coal, petroleum, varnishes, etc., are described. Lists are given of what are commonly called explosives, and of such substances as under abnormal conditions become inflammable and explosive; in the case of "dangerous liquids" the flashing point, inflammation point and "relative degree of danger" are given. The risk introduced by the use of bull's-eyes in sky-lights and on board ships, and the consequent focusing of the sun's rays on inflammable material, is pointed out. These are, of course, but a few of the subjects treated.

The book is clear, well written, and, so far as examined, accurate. Where purely chemical matters are discussed, facts are stated simply, and the author wisely refrains from using chemical symbols, a stand which the majority of writers of popular works would do well to take. To the chemist this dictionary cannot fail to be of interest, and to those engaged in the business of insurance it would seem to be indispensable. W. W. R.

OUTLINES OF GENERAL CHEMISTRY. By WILHELM OSTWALD. Translated, with the author's sanction, by JAMES WALKER, D. Sc., Ph. D. London: Macmillan & Co., 1890. xii + 396 pp. 8vo. Price, 10/ net.

This is a translation of Prof. Ostwald's recently-published "Grundriss der allgemeinen Chemie." That the work of translation has been accomplished in a scholarly manner will appear evident to any one examining the book; while as regards its accuracy, it will suffice to say that the proof-sheets all passed through the author's hands and were approved by him. W. W. R.

DIE EISENGALLUSTINTEN. Grundlagen zu ihrer Beurtheilung. Von O. SCHLUTTIG und G. S. NEUMANN. Dresden: v. Zahn & Jaensch, 1890. 97 pp. 8vo.

This book seems to be a very full treatise upon the subject of the iron-inks. The authors are chemists employed in the ink manufactory of Leonhardi, near Dresden, one of the largest establishments devoted to this industry in the world. They discuss the history of the manufacture of iron-inks; the legislation enacted by the Prussian Government looking to the employment of iron- rather than aniline- or chrome-inks; the advantages of the

former; the chemical process connected with their use; the various ingredients which go to make up the best inks, and the proportions in which these should be used; the classification of inks; the question of governmental inspection of inks, and the standards to be used in such inspection, etc. To a certain extent the book is controversial; nevertheless there is much contained in it which must prove of permanent value. W. W. R.

A Compend of Chemistry, Inorganic and Organic, including Urinary Analysis. By Henry Leffmann, M. D. Third Edition, Revised. Philadelphia: P. Blakiston, Son & Co., 1890. 193 pp. 12mo.

In the preface the author says: "Books of this class do not always meet with favor at the hands of reviewers; but any one who has had experience in teaching at American medical colleges knows that as long as the present methods continue some such assistance is absolutely essential." With reference to the last clause one cannot help the remark "The more's the pity." Whatever else may be said of the book, it is certainly true that a medical student cannot learn chemistry by its aid. He may learn to make statements about such subjects as Valency and Radicles; but of what use is this to him or to anybody else? There is altogether too much in the book for the poor medical student. If all the purely theoretical matter had been omitted there would be less chance of harm being done. That this book, or something like it, is in demand is a most melancholy fact. W. W. R.

Principles of General Organic Chemistry. By Prof. E. Hjelt, Helsingfors. Translated from the Author's German edition of the original work, by J. Bishop Tingle, Ph. D., F. C. S., Assistant in the Laboratory of the Heriot-Watt College, Edinburgh. Longmans, Green & Co.: London and New York, 1890. 220 pp. 8vo.

Professor Hjelt's book "is intended for those students who have already some general elementary knowledge of organic chemistry, and who wish to extend and *systematise* that knowledge." Part I has to deal with the composition, constitution, and classification of organic compounds; Part II is devoted to illustrating the connection between the constitution of organic compounds and their chief physical properties; while Part III deals with the chemical behavior of organic compounds. In this Part the order of treatment is determined by the result of the reaction, and not the action of the reagent. The last is the most interesting division of the book. In it are discussed such subjects as the following: Oxidation, Reduction, Dehydration, Splitting off of Halogen Hydrides, Hydration processes, Union of Carbon with Carbon, Disruption of Carbon Bonds, etc. Each subject is treated simply and clearly, and the book cannot fail to prove interesting and profitable to students of chemistry. I. R.

LESSONS IN ELEMENTARY CHEMISTRY, INORGANIC AND ORGANIC. By SIR HENRY E. ROSCOE, Emeritus Professor of Chemistry in Owens College, Manchester. New Edition, revised. London and New York: Macmillan & Co., 1890. 460 pp. 12mo.

This new edition of Roscoe's well-known book was prepared in 1885. In the preface, dated July, 1885, the author says: "In this edition, wholly reprinted, I have endeavored to place before the student all the important additions to the science which have been made since the last reprint. In the organic portion of the work, the necessary changes and additions are of greater extent than those in the less progressive inorganic department of the science." Any comment on the general character of this book would be superfluous, as it is familiar to all chemists. It is clear and succinct to a remarkable degree. While the succinctness is an advantage in so far as the book may be used for reference, it is, in the opinion of the writer of this notice, a decided disadvantage, in so far as the book is to be used for the purpose of studying chemistry. This is not so noticeable in the inorganic portion, but it is marked in the organic portion. So much is presented here that it is impossible to treat each subject satisfactorily. However, as an elementary presentation of the fundamental facts of chemistry the book is probably unsurpassed.

I. R.

SUGAR ANALYSIS. For Refiners, Sugar-Houses, Experimental Stations, etc., and as a Handbook of Instruction in Schools of Chemical Technology. By F. G. WIECHMANN, Ph. D., Instructor in Chemical Physics and Chemical Philosophy, School of Mines, Columbia College; Consulting Chemist to the Havemeyers and Elder Sugar Refining Company, Brooklyn, N. Y. Wiley & Sons, New York, 1890. 187 pp.

To those in need of a concise, clear account of the methods of sugar analysis this book can be cordially recommended. According to the author, who has had much excellent practice in the line of work of which he treats, "the schemes selected and here offered, embrace those methods of analysis which, after careful investigation, and, in many cases, after prolonged trial in practice, have seemed to the writer best adapted to the requirements of a technical laboratory." References to original articles are given throughout the book, and at the end there is a list of books and of periodical literature bearing on Sugar Analysis. It would seem that the book contains everything that is likely to be needed by those for whom it is intended, and as the matter is presented in an orderly and clear way, the book must prove extremely useful.

I. R.